A criterion for microphase separation in segmented polyurethane and polyurethane ureas

V. A. Vilensky and Y. S. Lipatov*
Institute of Macromolecular Chemistry, Academy of Sciences of Ukraine, 253160, Kiev, Ukraine
(Received 10 February 1993; revised 16 November 1993)

A criterion for microphase separation in segmented polyurethanes and poly(urethane urea)s is proposed. The existence of correlation between the ratios $\chi_{hs}/(\chi_{hs})_{cr}$ and the degree of segregation (α_{seg}) was established, where χ_{hs} is the thermodynamic interaction parameter between soft and hard blocks, calculated from the solubility parameters, and $(\chi_{hs})_{cr}$ is its critical value, calculated using the Scott equation. Correlation between the ratio $\chi_{hs}/(\chi_{hs})_{cr}$, the degree of segregation α_{seg} and the flexibility parameter σ was also found.

(Keywords: segmented polyurethanes; microphase separation; degree of segregation)

INTRODUCTION

Microphase segregation in polyurethane, resulting from the thermodynamic incompatibility (immiscibility) of 'hard' (h) and 'soft' (s) segments, has been well studied by many experimental techniques[1–5]. Interest in studying microphase separation stems from the fact that the ensuing physical network, whose crosslinks are aggregates of hard segments (rigid domains), determines to a great extent the mechanical and thermophysical properties of block copolyurethane (BCU).

This makes it necessary to find criteria for phase separation in BCU to establish correlations between the degree of segregation (α_{seg}) and thermodynamic, thermophysical, dynamic mechanical and other characteristics of BCU[6–8].

Bonart[8] was the first to introduce the concept of degree of segregation for segmented polyurethanes as a value characterizing incomplete phase separation in a system consisting of two thermodynamically immiscible species. The aim of this paper is to find a criterion connecting the thermodynamic parameters of a system with its degree of microphase separation.

EXPERIMENTAL

Table 1 contains data on the chemical structure and some characteristics of soft and hard segments, which allow one to calculate the interaction parameters χ_{hs} and $(\chi_{hs})_{cr}$; χ_{hs} is the thermodynamic interaction parameter between hard and soft segments, calculated from solubility parameters, and $(\chi_{hs})_{cr}$ is its critical value, calculated using the Scott equation. On this basis the compatibility of soft and hard segments may be theoretically evaluated.

The polymer samples (*Table 1*) have been synthesized using a two-stage method in 20% solution in dimethylformamide (DMF). In the first stage, a prepolymer with end isocyanate groups was obtained; the ratio of oligoester(oligoether)/diisocyanate was constant and equal to 1:2. The synthesis was performed at 60–70°C for 40–60 min. The consumption of isocyanate groups in the reaction of urethane formation was followed by i.r. measurements using the absorption band at 1720–1730 cm^{-1}. In the second stage, the hard segments have been extended by bifunctional compounds (diols, diamines, dihydrazides of dicarbonic acids, etc.). The reaction was performed at 80–90°C for 120–130 min. The end of the reaction also was followed by i.r. spectra.

The polyurethane and poly(urethane urea) films were cast from solution on an inert support (polytetrafluoroethylene) and dried at 60°C till film formation. Then the films were dried in vacuum at 90°C to constant weight. The samples were then stored for physical ageing at 20–25°C for 6 months to reach a standard state. Comparison of the morphological structure of samples investigated after 1 week and 1, 3, 6, 9 and 12 months has shown no detectable changes in their structure after 6 months.

The degree of segregation was estimated from data on small-angle X-ray scattering according to Bonart[8]:

$$\alpha_{seg} = \overline{\Delta\rho^2_{exp}}/\overline{\Delta\rho^2_{theor}} \qquad (1)$$

Here $\overline{\Delta\rho^2_{exp}}$ is the experimental value of the mean-square difference of electron densities of hard and soft blocks and $\overline{\Delta\rho^2_{theor}}$ is the mean-square difference of electron densities of the same blocks calculated theoretically.

The same parameter α_{seg} may be calculated from the jump in specific heat capacity at the glass transition using the d.s.c. method. Usually, to calculate the segregation, the equation proposed by Camberlin[9] is used:

$$\alpha_{seg} = \Delta C_{p,sb}/\Delta C_{p,olig} \qquad (2)$$

Here $\Delta C_{p,sb}$ is the heat capacity change at the glass–liquid transition of the soft blocks and $\Delta C_{p,olig}$ is the same for

---

* To whom correspondence should be addressed

0032-3861/94/14/3069–06

Table 1 Characteristics of the soft and hard blocks

Compositions of blocks[a]	MW ($g\,mol^{-1}$)	V_r ($cm^3\,mol^{-1}$)	ρ_{PU} ($g\,cm^{-3}$)	δ ($(cal\,cm^{-3})^{1/2}$)	σ
DPhMDI + BD + DPhMDI	608	521.8	1.165	10.96	2.10
DPhMDI + DHIPhA + DPhMDI	712	538.8	1.220	12.00	2.22
DPhMDI + BOMPh + DPhMDI	672	552.5	1.218	12.70	2.08
DPhMDI + NMDEA + DPhMDI	620	498.7	1.243	11.10	2.06
DPhMDI + DPhMAI	492	425.6	1.156	11.24	2.30
DPhMDI + BOMPh + DPhMDI + BOEAMPh + DPhMDI	1197	994.0	1.186	12.52	–
DPhMDI + BOMPh + DPhMDI + NMDEA + DPhMDI	1077	911.5	1.182	12.36	1.94
DPhMDI + BOMPh + NMDEA + BOEAMPh + DPhMDI	1086	1432.3	1.179	12.65	–
DPhMDI + NMDEA + DPhMDI + DHIPhA + DPhMDI	1081	917.7	1.178	11.35	2.08
TDI + DHIPhA + TDI	560	431.6	1.297	12.12	2.16
TDI + BD + TDI	456	367.1	1.242	11.18	–
TDI + TDAI	297	270.9	1.096	11.69	2.10
HMDI + DAPA + HMDI + DHIPhA + HMDI	959	729.4	1.314	12.63	–
HMDI + DAPA + HMDI + DHSA + HMDI	1108	869.9	1.274	12.01	–
HMDI + DAPA + HMDI + EDA + HMDI	765	572.0	1.341	12.36	–
HMDI + DAPA + HMDI + HH + HMDI	712	507.2	1.404	12.91	2.25
DPhMDI + DPhP + DPhMDI	747	643.7	1.160	10.87	2.11
DPhODI + BD + DPhODI	612	505.9	1.210	11.06	–
DPhMDI + DPhMDA + DPhMDI	716	627.4	1.141	11.17	–
TDI + DPhMDA + TDI	564	462.3	1.220	11.67	1.98
DPhMDI + DOEDS + DPhMDI	672	554.3	1.212	10.98	–
DPhMDI + EG + DPhMDI	580	488.9	1.186	–	–
DPhMDI + HD + DPhMDI	636	554.7	1.147	–	–
OEG	400	41.4	1.074	8.12	1.45
	600	–	–	–	1.45
	1000	–	–	–	1.46
	1500	–	–	–	1.47
OPG	1000	57.6	1.006	7.73	1.525
	2000	–	–	–	1.527
	3000	–	–	–	1.529
OTMG	1000	74.3	0.959	8.10	1.550
	2000	–	–	–	1.560
ODEGA	800	189.7	1.139	9.25	1.584
	1950	–	–	–	1.600
OBGA	1000	189.3	1.106	9.27	1.620
	2000	–	–	–	1.630

[a] Abbreviations are as follows:

BD	butanediol
BOMPh	bis(oxymethyl phosphonate)
BOEAMPh	bis(oxyethylaminomethyl)phosphonate
DAPA	pyromellitic acid dianhydride
DHIPha	isophthalic acid dihydrazide
DHSA	sebacinic acid dihydrazide
DOEDS	dioxyethyl disulfite
DPhMDA	diphenylmethanediamine
DPhMDI	diphenylmethane diisocyanate
DPhMAI	diphenylmethanamine isocyanate
DPhODI	diphenyloxide diisocyanate
DPhP	diphenylpropane
EDA	ethylenediamine
EG	ethylene glycol
HD	hexanediol
HH	hydrazine hydrate
HMDI	hexamethylene diisocyanate
NMDEA	*N*-methyldiethanolamine
OBGA	oligobutylene glycol adipate
ODEGA	oligodiethylene glycol adipate
OEG	oligoethylene glycol
OPG	oligopropylene glycol
OTMG	oligotetramethylene glycol
TDAI	2,4-tolueneamine isocyanate
TDI	2,4-toluene diisocyanate

pure oligomer playing the role of soft segments in urethane polymers. This equation does not take into account that $C_{p,sb} > C_{p,olig}$ (refs. 8, 11) because of the greater free volume of soft blocks in segmented polyurethanes as compared with pure oligomer[18]. Neglecting this fact often leads to unreliable values of α_{seg} (for example, in some cases $\alpha_{seg} > 1$[11]). To estimate α_{seg} we propose to introduce into equation (2) the proportionality coefficient K_s and normalize $\Delta C_{p,sb}$ by volume fraction of soft block in segmented polymers (ϕ_{sb}). The K_s value is supposed to be determined by the volume and molecular mass of the repeat unit in BCU and by its density. For this purpose we can use the packing parameter proposed by Askadsky[22]:

$$K_s = (N_A \sum \Delta V_{ru})/(M_{ru}/\rho_{BCU}) \tag{3}$$

where N_A is the Avogadro number, ΔV_{ru} is the volume of the repeat unit in the polymer, M_{ru} is the molecular mass of the same unit and ρ_{BCU} is the experimental density of BCU.

In this case equation (2) acquires the form:

$$\alpha_{seg} = [\Delta C_{p,sb}/(\Delta C_{p,olig}\phi_{sb})]K_s \tag{4}$$

As the K_s values depend on the chemical structure and change in the interval 0.63–0.68, it is evident that this coefficient does not influence the character of the dependences of α_{seg} on the polymer structure. The values of α_{seg} calculated from equation (4) were in agreement with α_{seg} estimated from SAXS.

RESULTS

To gain some insight into the problem, we have used experimental data on degree of segregation for many segmented polyurethanes and poly(urethane urea)s obtained by us and others[7–14]. We assume that there should be a correlation between the degree of segregation and the thermodynamic interaction parameter χ_{hs}. The thermodynamic interaction parameters of soft and hard blocks in BCU have been calculated using data on the solubility parameters according to the equation[15]:

$$\chi_{hs} = (V_r/RT)(\delta_s - \delta_h)^2 \tag{5}$$

Here V_r is the molar volume of the BCU block having the smallest repeat unit, usually the molar volume of the soft block, R and T are respectively the universal gas constant (8.3144 J mol^{-1} K^{-1}) and thermodynamic temperature, and δ_s and δ_h are the solubility parameters of the soft and hard blocks respectively, calculated according to refs. 15 and 14.

To calculate the critical values of the interaction parameter, we have used the Scott equation[17]:

$$(\chi_{hs})_{cr} = (x_h^{-1/2} + x_s^{-1/2})/2 \tag{6}$$

where x_s and x_h are respectively the degree of polymerization of the soft and hard blocks in BCU. These values have been calculated for all the polyurethanes under investigation having the general formula:

$$(AB)_n = [(a_0)_{x_s}(b_0)_{x_h}]_n \tag{7}$$

where a_0 and b_0 are respectively the repeat units of oligoester (ether) and hard blocks, and

$$x_s = M_A/M_{0A} \qquad x_h = M_B/M_{0B} \tag{8}$$

where M_A and M_B are the molecular masses of blocks A and B, and M_{0A} and M_{0B} are the molecular masses of the repeat unit soft and hard blocks.

When x_h is equal to 1, to calculate $(\chi_{hs})_{cr}$ we have used the expression $x_h = M_B/100$, which, according to Krause[24], gives a good agreement with equation (8) for degree of polymerization of hard blocks.

According to Krause[24] the parameters χ_{AB} and $(\chi_{AB})_{cr}$ are correlated by the following inequalities, determining the state of a polymer–polymer system:

$$\begin{array}{ll} \chi_{AB} > (\chi_{AB})_{cr} & \text{the system is unstable and separates into two phases} \\ \chi_{AB} < (\chi_{AB})_{cr} & \text{the system is stable} \end{array} \tag{9}$$

We have found that, at 298 K for the BCU and block copoly(urethane urea) (BCUU), χ_{hs} is always much higher than $(\chi_{hs})_{cr}$, that is

$$\chi_{hs} \gg (\chi_{hs})_{cr} \tag{10}$$

This means that the blocks of more than 120 urethane-containing polymers of different structure studied by us should be immiscible, while complete separation is impossible because of the covalent bonding of the blocks. This is confirmed by X-ray scattering and calorimetric[7,8,10–13] studies, which have shown the interval of α_{seg} variation in BCU and BCUU to be within ~0.2–0.7. We consider that segregation of the immiscible blocks occurs only for those polymers whose structure is close to the equilibrium state. As BCU is a two-phase system, as the equilibrium state at constant temperature and pressure such a state was taken where:

$$\Delta\alpha_{seg}|_{t=t_i} = 0 \tag{11}$$

t_i being found from testing a specimen of the polymer (see 'Experimental' part).

From equation (5), it follows that with decreasing temperature the calculated values χ_{hs} become higher, as the urethane block copolymers have an upper critical solution temperature. It is worth noting that the condition:

$$\chi_{hs} = (\chi_{hs})_{cr} \quad \text{or} \quad \chi_{hs}/(\chi_{hs})_{cr} = 1 \tag{12}$$

which corresponds to the transition of a polymer–polymer system from a stable to a metastable state, has not previously been considered. The parameter $(\chi_{hs})_{cr}$ in equation (6) depends on the degree of polymerization and corresponds to the critical point in the phase diagram. Simultaneously, the values of parameters χ_{hs} in equation (5) are dependent on δ_i, V_r and T. Thus, the inequalities:

$$\chi_{hs}/(\chi_{hs})_{cr} < 1 \tag{13}$$

and

$$\chi_{hs}/(\chi_{hs})_{cr} > 1 \tag{14}$$

make it possible to judge where in the phase diagram region a system is placed. The calculated values of χ_{hs} and $(\chi_{hs})_{cr}$ and experimental values of the degree of segregation for BCU and BCUU are given in *Tables 2–4*. There are no correlations between values of the interaction parameters χ_{hs}, $(\chi_{hs})_{cr}$ and α_{seg}. However, if we compare the change of the ratio $\chi_{hs}/(\chi_{hs})_{cr}$ with α_{seg}, their interconnection becomes evident. The corresponding dependencies for the series of polymers with various chemical structure of soft or hard blocks are presented in *Figures 1–3*. Microphase separation in BCU is known to proceed independently of whether these BCU are based on oligoether or oligoester. At the same time it has been

Table 2 Correlation between $\chi_{hs}/(\chi_{hs})_{cr}$ and degree of segregation (α_{seg}) of blocks in segmented polyurethane ureas[23]

Hard block	Soft block	χ_{hs}	$(\chi_{hs})_{cr}$	$\chi_{hs}/(\chi_{hs})_{cr}$	α_{seg}[a]
DPhMDI + DPhMAI	OTMG-1050	1.304	0.274	4.76	0.56
	OTMG-2000	1.304	0.207	6.30	0.59
	ODEGA-800	1.337	0.493	2.71	0.52
	ODEGA-1540	1.337	0.350	3.82	0.57
TDI + TDAI	OTMG-1050	1.702	0.378	4.50	0.48
	OTMG-2000	1.702	0.299	5.69	0.54
	ODEGA-800	2.010	0.630	3.19	0.42
	ODEGA-1540	2.010	0.467	4.30	0.50

[a] All the data on α_{seg} have been obtained by the d.s.c. method

Table 3 Correlation between $\chi_{hs}/(\chi_{hs})_{cr}$ and degree of segregation (α_{seg}) in segmented polyurethanes and poly(urethane semicarbazide)s[20]

Hard block	Soft block	χ_{hs}	$(\chi_{hs})_{cr}$	$\chi_{hs}/(\chi_{hs})_{cr}$	α_{seg}[a]
DPhMDI + DPhP + DPhMDI	OTMG-1000	1.01	0.233	4.34	0.21
DPhMDI + BD + DPhMDI		1.08	0.245	4.41	0.24
DPhODI + BD + DPhODI		1.16	0.240	4.83	0.32
DPhMDI + DOEDS + DPhMDI		1.09	0.212	5.14	0.53
DPhMDI + DHIPhA + DPhMDI	OEG-400	1.13	0.249	4.54	0.33
	OEG-600	1.13	0.209	5.41	0.37
	OEG-1000	1.13	0.171	6.61	0.45
	OEG-1400	1.13	0.129	8.76	0.51
TDI + DHIPhA + TDI	OEG-400	1.18	0.284	4.15	0.21
	OEG-1000	1.18	0.200	5.90	0.29
	OEG-1400	1.18	0.176	6.70	0.37

[a] All α_{seg} values have been found by d.s.c. method

Table 4 Correlation between $\chi_{hs}/(\chi_{hs})_{cr}$ and α_{seg} in segmented poly(urethane urea)s and poly(urethane semicarbazide)s[11-13]

Hard block[b]	Soft block	χ_{hs}	$(\chi_{hs})_{cr}$	$\chi_{hs}/(\chi_{hs})_{cr}$	α_{seg}[a]
DPhMDI + PhDA + DPhMDI	OEG-1030	0.69	0.172	3.99	0.42
DPhMDI + DPhMDA + DPhMDI		0.83	0.189	4.41	0.43
DPhMDI + DHIPhA + DPhMDI		1.11	0.171	6.49	0.47
DPhMDI + DPhMDA + DPhMDI	OPG-1450	1.21	0.164	7.40	0.61
DPhMDI + DHIPhA + DPhMDI		1.87	0.165	11.33	0.73
DPhMDI + DH(R)SUDI + DPhMDI ($R=C_6H_{13}$)	OTMG-1030	0.99	0.199	4.98	0.70
DPhMDI + DHSUA + DPhMDI		1.32	0.220	6.00	0.84
TDI + (CN)EDA + $TDI_{x=1}$	OTMG-1030	2.56	0.268	9.56	0.56
TDI + (CN)EDA + $TDI_{x=3}$		2.56	0.143	17.85	0.67

[a] All the α_{seg} values have been determined from small-angle X-ray scattering

[b] Abbreviations:

PhDA, phenylene diamine	DHS, dihydrazide sulfosuccinic acid
DH(R)S, dihydrazide-R-sulfosuccinic acid	(CN)EDA, cyane ethylated ethylene diamine

ascertained that phase separation in BCU based on an oligoether proceeds deeper[19]. The existence of a specific interaction between urethane and ester groups impedes the separation processes. This fact predetermined the necessity for analysing the behaviour of $\chi_{hs}/(\chi_{hs})_{cr}=f(\alpha_{seg})$ depending on the oligoether or oligoester nature of the BCU component. The results of the analysis are shown in *Figure 1*. The successively increasing polarity of the hard blocks by introducing into them, along with urethane, also urea and bis-semicarbazide groups for oligoether-based (oligotetramethylene glycol, $MW=1000$) polymers, leads to an increase in the slope of the dependence $\chi_{hs}/(\chi_{hs})_{cr}=f(\alpha_{seg})$. For polymers based on the oligoester (oligobutylene glycol adipate, $MW=2000$), this dependence (line 2) is inversely proportional and represents the strengthening of interactions between soft and hard blocks.

Figure 2 demonstrates that a correlation between

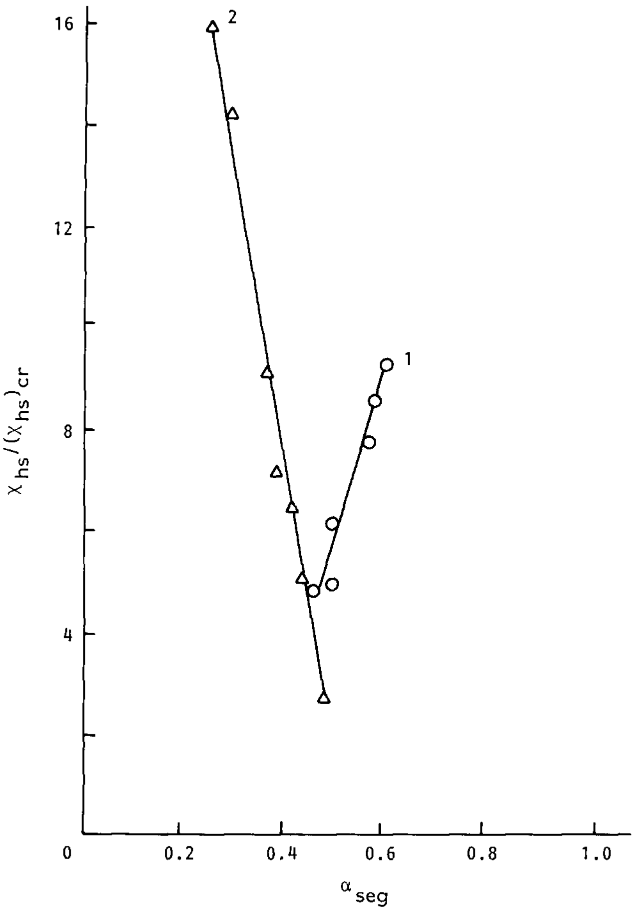

Figure 1 Plot of $\chi_{hs}/(\chi_{hs})_{cr}$ as a function of the degree of segregation in urethane block copolymers: BCU based on OTMG-1000 (1); BCU based on OBGA-2000 (2)

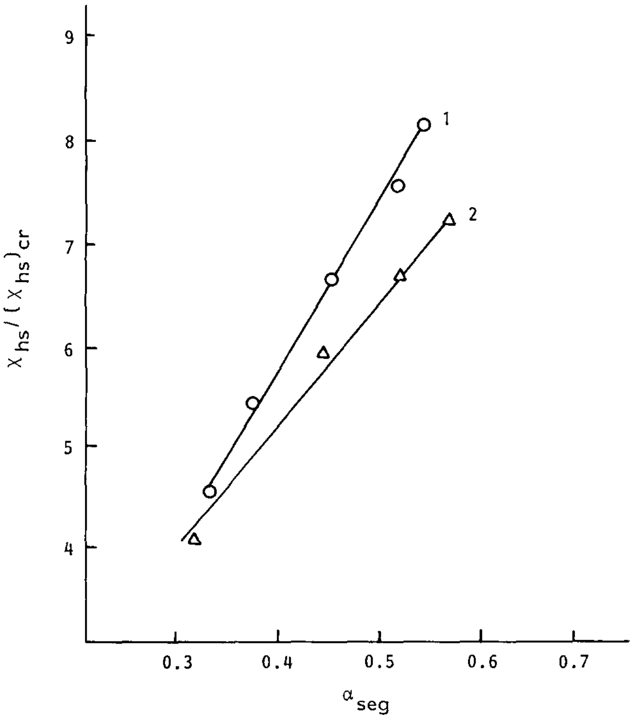

Figure 2 Plot of $\chi_{hs}/(\chi_{hs})_{cr}$ as a function of the degree of segregation in bis-semicarbazides based on OEG of different *MW*: BCU based on DPhMDI (1); BCU based on TDI (2)

$\chi_{hs}/(\chi_{hs})_{cr}$ and α_{seg} also exists for polyurethane differing in the structure of the diisocyanate fragment of the hard blocks. A smaller slope of line 2 as compared with line 1 indicates that the proposed criterion predicts a decrease in the segregation of soft blocks with impaired symmetry of diisocyanate in hard blocks, which indeed occurs in BCU when 4,4-diphenylmethane diisocyanate is substituted with 2,4-toluene diisocyanate[19].

Earlier[20] we have shown for the first time the important role played by the thermodynamic flexibility of the blocks in microphase separation. In this study we have shown for the first time the important role played by the calculated thermodynamic equilibrium flexibility parameters σ_{sb} and σ_{hb}—for soft and hard blocks respectively—for polymers based on oligoethylene glycol (*MW* = 400–1400), oligopropylene glycol (*MW* = 1000–3000) and oligotetramethylene glycol (*MW* = 1000, 2000). The equilibrium flexibility of every polymer block was calculated by the equation[21]:

$$\sigma^2 = \langle \overline{h_\theta^2} \rangle / 2n\bar{l}^2 \tag{15}$$

where $\langle \overline{h_\theta^2} \rangle$ is the mean-square distance between the ends of an undisturbed chain, n is the number of bonds in the chain of primary valences, and $\bar{l}$ is the average length of the bond in the chain of primary valences.

The data presented in refs. 8, 10–13 allow one to calculate the flexibility parameters of the segments forming BCU and BCUU and to compare them with α_{seg} and the ratio $\chi_{hs}/(\chi_{hs})_{cr}$. It happens that these characteristics are interconnected. *Figure 3* shows that the values σ_{sb} of the oligoester fragment determine the slope of the function $\chi_{hs}/(\chi_{hs})_{cr} = f(\alpha_{seg})$. As is seen from *Figure 4*, the increase of the parameter σ_{hb} results in the growth of the degree of segregation of the soft blocks. This conclusion is valid for BCU based both on oligoether (oligotetramethylene glycol) and on oligoester (oligobutylene glycol adipate). Linear σ_{hb} vs. α_{seg} and $\chi_{hs}/(\chi_{hs})_{cr}$ vs. α_{seg} relations make it possible to connect all the parameters influencing the microphase separation process.

Figure 5 presents a three-dimensional dependence of the degree of segregation and flexibility parameters σ_{sb} and σ_{hb} of a block copolyurethane. It is seen that α_{seg} surface curvature has no pronounced extrema, and hence the possibility for predicting the degree of segregation with varying flexibility parameters is retained.

CONCLUSION

The analysis of the variation of the $\chi_{hs}/(\chi_{hs})_{cr}$ ratio and of the degree of segregation of the blocks in segmented polyurethanes, poly(urethane urea)s and poly(urethane semicarbazide)s has demonstrated the existence of a linear correlation between these characteristics. This makes it possible to calculate the expected microphase separation for any segmented polymers with arbitrary predetermined structure and molecular weights of soft and hard blocks. It has also been shown that the equilibrium flexibility parameters σ_{sb} and σ_{hb} affect the segregation processes ambiguously.

Simultaneously one should have in mind that in real BCU the degree of segregation attained during microphase separation depends on its condition (temperature range, rate of temperature changing, etc.), and that the considerations presented here may not be valid for all systems, preserving their general meaning for description

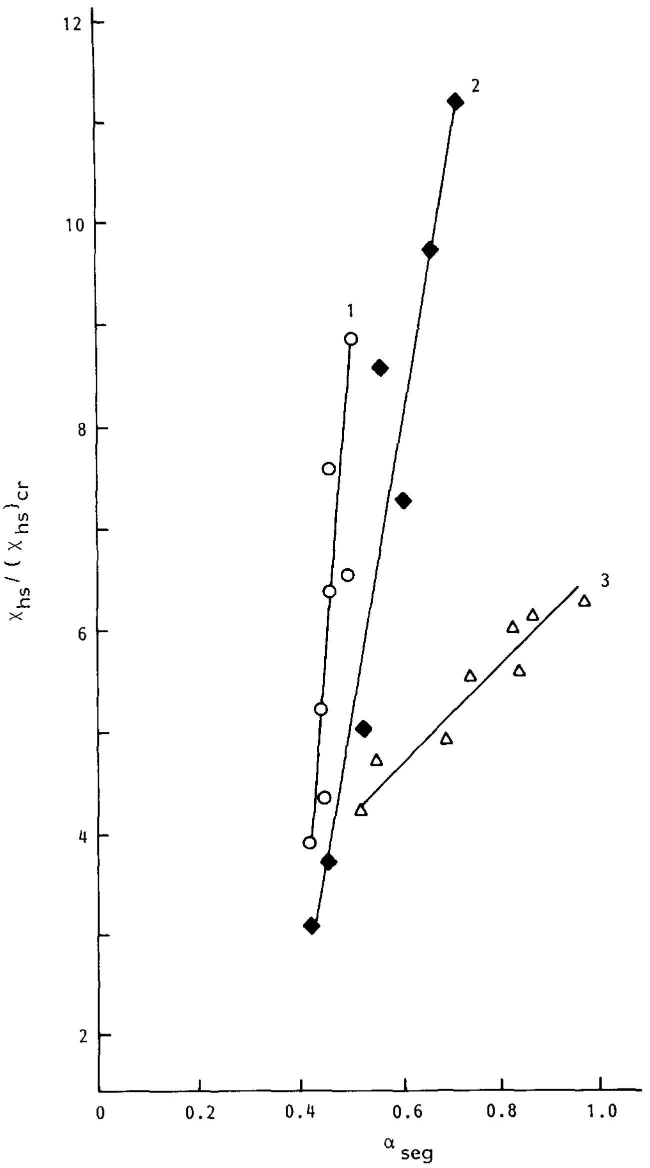

Figure 3 Plot of $\chi_{hs}/(\chi_{hs})_{cr}$ as a function of the degree of segregation in urethanes and urethane ureas based on the oligoesters: OEG (1), OPG (2) and OTMG (3)

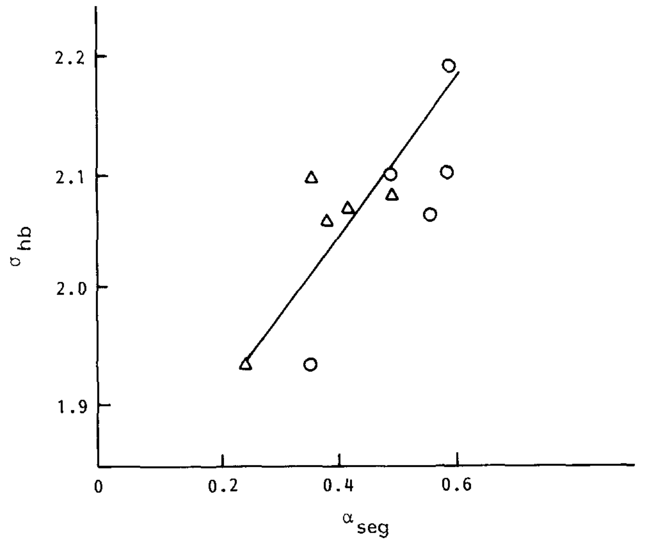

Figure 4 Degree of segregation as a function of parameter σ of hard blocks of BCU based on OTMG (1) or OBGA (2)

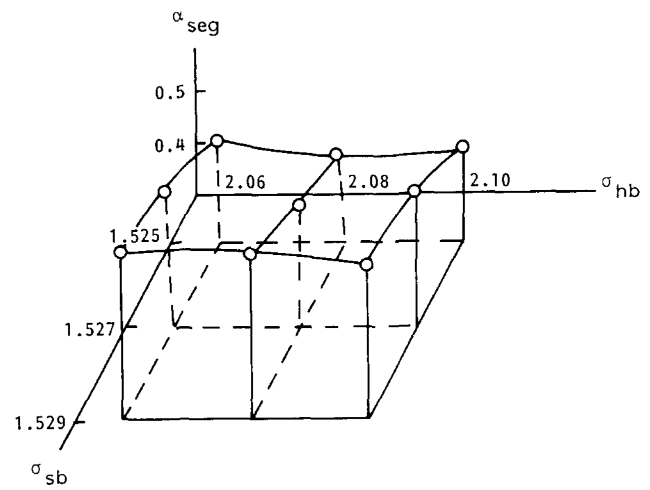

Figure 5 Degree of segregation as a function of parameters σ of hard and soft blocks of BCU based on OPG

of the interconnection between degree of segregation and thermodynamic state of the polymer.

REFERENCES

1 Koutsky, J. A., Hein, N. V. and Cooper, S. L. *J. Polym. Sci. (B)* 1970, **8**, 353
2 Vilensky, V. A., Kercha, Y. Y., Lipatov, Y. S. *et al. Dokl. Akad. Nauk SSSR* 1977, **232**, 81
3 Semich, G. A. and Macknight, W. J. *Adv. Polym. Ser.* 1979, **176**, 97
4 Wilkes, C. and Jusek, C. *J. Macromol. Sci., Polym. Phys. (B)* 1973, **7**, 157
5 Dumeins, J., Jelinsky, L., Leung, L. *et al. Macromolecules* 1985, **18**, 116
6 Camberlin, Y. and Pascault, J. P. *J. Polym. Sci., Polym. Phys. (B)* 1983, **21**, 415
7 Vilensky, V. A., Kercha, Y. Y., Lipatov, Y. S. *et al. Vysokomol. Soed. (A)* 1986, **28**, 1259
8 Bonart, R. and Muller, E. H. *J. Macromol. Sci. (B)* 1974, **10**, 177
9 Camberlin, Y. and Pascault, J. P. *J. Polym. Sci., Polym. Phys. (B)* 1984, **22**, 1834
10 Petrovich, Z. S. and Javni, I. *J. Polym. Sci., Polym. Phys. (B)* 1989, **27**, 545
11 Shilov, V. V., Lipatov, Y. S. and Bogdanovich, V. P. *Kompoz. Polym. Mater. SSSR* 1981, **11**, 13
12 Navrotskaya, R., Grekov, A. P. and Gomza, Y. P. *Kompoz. Polym. Mater. SSSR* 1960, **44**, 61
13 Vorona, V., Shevchuk, A. and Shilov, V. V. *Kompoz. Polym. Mater. SSSR* 1988, **39**, 20
14 'Polymer Blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. 1
15 Van Krevelen, D. W. 'Properties of Polymer Correlations With Chemical Structure', Elsevier, Amsterdam, 1972
16 Rosovitsky, V. F. and Lipatov, Y. S. *Dokl Akad. Nauk SSSR* 1985, **283**, 910
17 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279
18 Lipatov, Y. S. and Vilensky, V. A. *Vysokomol. Soed. (A)* 1975, **17**, 2069
19 Kercha, Y. Y. 'Physico-Chemistry of Polyurethanes', Naukova Dumka, Kiev, 1979
20 Vilensky, V. A., Kercha, Y. Y., Shtompel, V. I. *et al. Vysokomol. Soed. (A)* 1985, **27**, 1008
21 Privalko, V. P. 'Molecular Structure and Properties of Polymers', Khimija, Leningrad, 1986
22 Askadsky, A. A. and Matveev, Y. I. 'Chemical Structure and Physical Properties of Polymers', Khimija, Moscow, 1983
23 Vilensky, V. A., Lipatnikov, Y. N., Lipatnikov, N. A. and Kercha, Y. Y. *Kompoz. Polym. Mater. SSSR* 1990, **44**, 47
24 Krause, S. *J. Macromol. Sci.-Rev.* 1972, **C7**, 251