L. ŠIMEK*), J. DOSTÁL*), M. BOHDANECKÝ**)

Calculation of the [η] (*M*) relationship for ethylene/propylene copolymers from the relations for homopolymers

Summary — Intrinsic viscosity [η]—weight-average molecular weight (M_w) relations were calculated for ethylene/propylene copolymers at varying copolymer compositions by using the principle of the two-parameter theory of dilute polymer solutions and by taking the conformational and interaction parameters for PE and PP. The interaction parameter between chemically dissimilar monomer units was assumed to be zero. For high-temperature solvents [tetralin, trichlorobenzene (TCB), α-chloronaphthalene (α-CN)], the relation was found to be sensitive to copolymer composition. The calculated data proved to be consistent with the reported experimental data. The results were used for a theoretical examination of the effect of copolymer composition on the calibration of SEC columns.

Key words: ethylene/propylene copolymers, calculation of [η](*M*) function, calibration of SEC column.

Ethylene/propylene copolymers (EPM) and ethylene/propylene/diene terpolymers (EPDM) are among the most important elastomers [1—3]. Their properties and application strongly depend on their structure (composition and sequential arrangement of monomer units, branching), molecular weight and molecular weight distribution (*MWD*). When estimating the viscosity-average molecular weight (M_v) from the intrinsic viscosity [η] or using the universal calibration method [4] to estimate *MWD* by size exclusion chromatography (SEC), the composition dependence of the parameters *K* and *a* in the Mark—Houwink—Kuhn—Sakurada (MHKS) equation

$$[\eta] = K \cdot M_v^a \tag{1}$$

is needed. The usual method of estimation, *viz.*, correlation of the intrinsic viscosities [η] with molecular weights for a set of fractions of low molecular and compositional heterogeneity, is time consuming, laborious and less reliable than that for homopolymers.

This correlation is reliable only if the weight-average molecular weight M_w is used. Unfortunately, the estimation of M_w by light scattering is not easy with homopolymers of olefins and is very difficult and more inaccurate with commercial copolymers and terpolymers (*cf.* [1—3]). Therefore, in most papers, the EPM copolymers have been characterized by SEC or osmometry (number-average molecular weight M_n, [1—8]). In the former case, the result depends on the method used to calibrate the SEC columns. In the latter, polymolecularity effects on the correlation of [η] with M_n can overlap with the effect of composition and even overshadow it.

For these reasons, data for the dependence of the MHKS parameters on the composition of EPM copolymers are sparse in the literature [3, 9]. These difficulties explain the attempts at estimating the MHKS parameters for EPM copolymers from the data for polyethylene and polypropylene. Moraglio [9] has assumed the intrinsic viscosity of EPM copolymers to be obtainable by linear interpolation between those for homopolymers at the same molecular weight. The method was successful in some cases [1] but fallible in others [10]. Assuming short side chains (methyl groups in EPM) not to affect the conformation of the polyethylene backbone but only the mean molecular weight per monomer unit, Scholte *et al.* [11] calculated the *K constant* for copolymers from the K_{PE} value for polyethylene as:

$$K = K_{PE} \cdot (1 - w_P) \tag{2}$$

where: *w_P is the weight fraction of propylene units.*

In this paper another possibility is examined. The starting point is the two-parameter theory of dilute polymer solutions and the characteristic parameters (unperturbed chain dimensions and polymer-solvent interaction parameters) for homopolymers. The results of calculations are checked against the logarithmic plots of [η] *vs.* M_w for copolymers reported in the literature.

---

*) Faculty of Technology, Tomas Bata University, 762 72 Zlin, Czech Republic.

**) Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic.

THEORETICAL BACKGROUND

The discussion in based on the semiempirical Yamakawa—Tanaka equation [12]

$$[\eta] = K_0 \cdot M^{1/2} + 0.346\,\Phi_{0,\infty} \cdot B \cdot M \qquad (3)$$

$$\text{where:}\, K_0 = \Phi_{0,\infty} \cdot (<R^2>_0/M)^{3/2}_{\infty} \qquad (4)$$

$\Phi_{0,\infty}$ *is the Flory viscosity constant for non-draining random coils unperturbed by the excluded-volume effect,* $<R^2>_0$ *is the mean-square end-to-end distance in the random coil limit, the B parameter is characteristic of the excluded-volume interaction of chain segments and depends on the polymer-solvent interaction.*

Eqn (3) is valid [12] for

$$\alpha^3_\eta = [\eta]/K_0 \cdot M^{1/2} < 2.5 \qquad (5)$$

where: α^3_η *is the viscosity radius expansion factor,* and fails at high values of α^3_η, *i.e.*, at high molecular weights and in good solvents.

The K_0 and B parameters reflect, respectively, the short-range and long-range interactions of chain units and depend on the copolymer composition [13—15]. If the $K_{0,i}$ values ($i = A, B$) for homopolymers meet the condition that $0.4 < K_{0,A}/K_{0,B} < 2.5$, the dependence of the constant K_0 on the weight fraction w_i of monomer units may be approximated by a linear function [15]

$$K_0 = K_{0,A} \cdot w_A + K_{0,B} \cdot w_B \qquad (6)$$

With some copolymers, however, the linearity fails to hold and an extra term ΔK_0 corresponding to short range interactions between unlike monomer units has to be introduced [16].

The B parameter of copolymers consists of three components B_{ij} corresponding to different types of long-range interactions between chain units. It is usually expressed as [13—15]

$$B = B_{AA}x_A + B_{BB}x_B + 2x_Ax_B\Delta B_{AB} \qquad (7)$$

where the extra term ΔB is:

$$\Delta B = B_{AB} - \frac{1}{2}(B_{AA} + B_{BB}) \qquad (8)$$

If B_{AB} is equal to the arithmetic mean of the B_{AA} and B_{BB} values, the B-parameter of the copolymer becomes a linear function of composition (mole fraction x_i of monomer units).

The B-parameter is related to the Flory—Huggins (χ) parameter of the free energy of dilution by the equations

$$B = \left(\frac{2\bar{v}^2}{V_1 N_A}\right) \cdot \left(\tfrac{1}{2} - \chi\right) \qquad (9)$$

$$\tfrac{1}{2} - \chi = \psi - \kappa \qquad (10)$$

where: ψ *and* κ *are, respectively, the entropy of dilution and the enthalpy of dilution parameters at infinite dilution,* $\bar{v}$ *is the partial polymer mole volume,* V_1 *is the solvent mole volume, and* N_A *is the Avogadro constant.* With copolymers, the χ-parameter consists of three components [15]

$$\chi = \chi_A x_A + \chi_B x_B - \chi_{AB} x_A x_B \qquad (11)$$

The combination of eqns. (9) and (11) gives

$$B = \left(2\bar{v}^2/V_1 \cdot N_A\right) \cdot \left[\frac{1}{2} - (\chi_A x_A + \chi_B x_B) + \chi_{AB} x_A x_B\right] \qquad (12)$$

If there is no preference for attractive or repulsive interactions of chemically dissimilar units, then χ_{AB} and ΔB are equal to zero, and the dependence of χ and B on the copolymer composition is linear. Preference for repulsive interactions ($\chi_{AB} > 0$) is indicated by negative deviations of χ and positive deviations of B from linearity, and vice versa.

The χ_{AB} parameter consists of an entropy and an enthalpy contribution

$$\chi_{AB} = \chi^s_{AB} + \chi^h_{AB} \qquad (13)$$

The entropic part is usually assumed to be small, and this assumption seems to be supported by the finding that, for most copolymers studied so far, the χ_{AB}-values were close to the enthalpy term computed from the solubility parameters δ_A and δ_B of the copolymer constituents according to

$$\chi^h_{AB} = (V_1/\mathrm{RT}) \cdot (\delta_A - \delta_B)^2 \qquad (14)$$

where *R is the gas constant and* T *is the temperature.*

The assumption that $\chi^s_{AB} = 0$ comes from the lattice theory of polymer solutions and shows mixing of unlike polymers to be associated with a negligible combinatorial entropy. Most values of χ_{AB} reported so far are low ($\chi_{AB} \cong 0.1$ [16]). We are aware of one exception from this rule. By analyzing the intrinsic viscosity data from Ref. [17] Staszewska *et al.* [18] found remarkably high values of χ_{AB} for ethylene/butylene copolymers (0.47, 0.61 and 0.64 in biphenyl, α-chloronaphthalene and *n*-dodecane, respectively) at temperatures around 140°C. These values strongly exceed the value $\chi^h_{AB} = 0.08$ calculated from the solubility parameters (16.6 and 17.8 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for polyethylene and polypropylene, resp. [19]). The difference has been attributed to an entropy effect ($\chi^s_{AB} > 0$). In view of the chemical similarity of EPM and EPB copolymers, it seems necessary to consider a similar effect with the former copolymers.

TREATMENT OF EXPERIMENTAL DATA

Experimental values of $[\eta]$ and M_w of PE and PP were taken from Refs. [20—27], those for EPM and EPDM copolymers from Refs. [2, 11]. The B-parameter of homopolymers was estimated from the slope of the plots of $[\eta]/M_w^{1/2}$ *vs.* $M_w^{1/2}$, according to eqn (3). The use of this equation was legitimate, because almost each α^3_η value was lower than 2.5. In some cases the scatter of data points was rather large, particularly with polyethylene if results from different laboratories were pooled. The B-values are listed in Table 1.

Table 1. Interaction parameters B*) of polyethylene and polypropylene

Solvent	Temp. °C	$B \cdot 10^{27}$	[η] (*M*) data in	Temp. °C	$B \cdot 10^{27}$	[η] (*M*) data in
	Polyethylene			Polypropylene (isotactic)		
Decalin	135	10.5	[20, 21]	135	9.5	[24—26]
Tetralin	120—130	11	[20, 22]	135	6.0	[27]
TCB*)	130	9.1	[23]	135	5.4	[27]
α-CN**)	125	7.2	[20]	145	2.4	[27]
	130	6.0	[23]			
	145	6.4	[22]			

*) Estimated as described in main text (Treatment of Experimental Data).

**) TCB = trichlorobenzene, α-CN = α-chloronaphthalene.

For linear polyethylene, the K_0-values have well been established in several Θ-solvents [28—32]. This is not the case with polypropylene. The value estimated by Kinsinger and Hughes [33] is higher than the recent K_0 ($0.9 \cdot 10^{-3}$ dL/g) estimated by linear extrapolation to 130°C of the log K_0 *vs.* T measured over 5—77°C [34]. The difference is presumably due to the effect of polymolecularity on the former result which has been obtained by using the number-average molecular weight. For EPM, the K_0-value (w_P = 0.6, Fig. 1) was obtained from the data measured at 5 to 61°C [35] in a similar way as for polypropylene. The other value, at w_P = 0.53, was taken from Ref. [6].

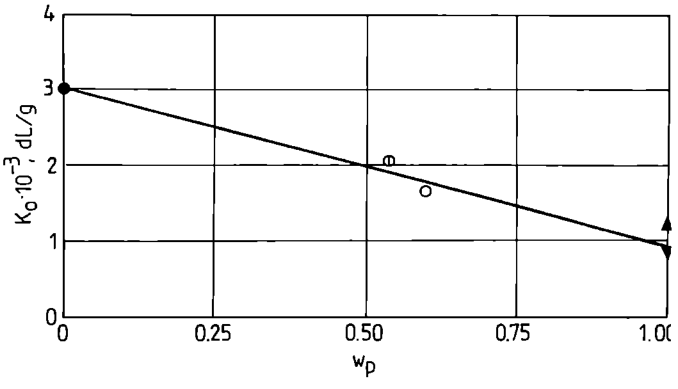

Fig. 1. K_0 vs. composition of EPM: w_P — weight fraction of propylene units; data points for PE — ● [32], PP — ▲ [33], ▼ [34—36], EPM — ⊘ [6], ○ [35—36]

Correlation of [η] with M_w for PEP copolymers

In principle, exact prediction of the [η] *vs.* M_w relationship for copolymers is possible only if the following data are known: (*i*) $K_{0,i}$ and B_{ii}-values and (*ii*) ΔK_0 and ΔB_{AB}. The data (*i*) are usually known or are easy to obtain whereas the (*ii*) are not. Therefore, a prediction for most copolymers can only be approximate as the ΔK_0 and ΔB_{AB} terms are neglected. As follows from eqns. (6)—(8) the sensitivity of the correlation of [η] *vs.* M_w to composition depends on the difference in the $K_{0,i}$ and B_{ii} values. In general, the variation in K_0 is more relevant in the low molecular weight region whereas the variation in *B* is more important at high molecular weights. The difference in K_0 is usually independent of the solvent, the differences in B_{ii} are solvent dependent. The sensitivity is expected to be stronger if the composition dependences exhibit the same trend in both parameters. In the opposite case, the dependence of [η] on M_w is less sensitive to composition, and a region may exist where the effect of composition is negligible.

The K_0-values of EPM copolymers decrease as the content of propylene units is increased (Fig. 1). For high temperature solvents, the *B*-parameters show the same trend (Table 1). Thus, the sensitivity on composition is expected to be larger with tetralin and trichlorobenzene. With decalin, the sensitivity is lower because the difference in *B*-values is low, though of the same sign as with the preceding solvents.

The assumption that the parameter ΔB_{AB} for ethylene and propylene segments is equal to zero has recently been confirmed by the results for solutions in benzene [37]. No data are available to confront it with high temperature solvents. Therefore, to assess the potential effect of this parameter, calculations were made with eqn. (7) and several values of ΔB_{AB}. The results of these calculations for trichlorobenzene (TCB) are displayed in Fig. 2. Those for other solvents are similar. It is seen that positive ΔB_{AB} values render the dependence of [η] on *M* steeper.

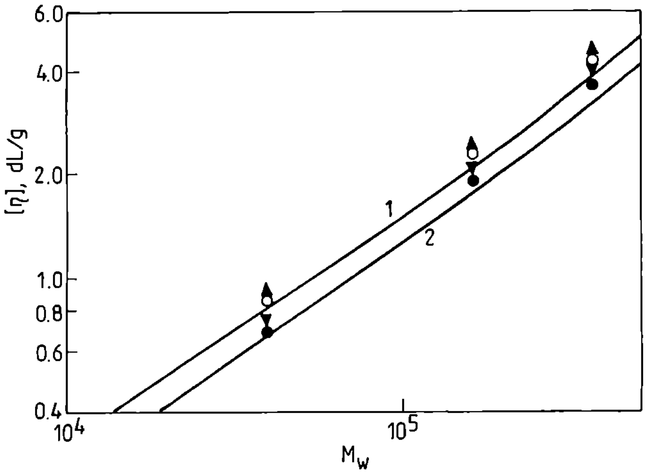

Fig. 2. Calculated relationships [η] vs. M_w for EPM in TCB at 130°C Curves 1 and 2 for $\Delta B_{AB} = 0$ and x_B = 0.2 and 0.5, respectively; points for $\Delta B_{AB} \cdot 10^{27} = 3$ [for x_B = 0.2 (○), 0.5 (●)] and 6 [for x_B = 0.2 (▲), 0.5(▼)]; x_B — mole fraction of propylene units

In Fig. 3, the calculated [η] *vs.* *M* relationships are tested against the experimental data where samples are characterized by M_w-values. The calculated relation-

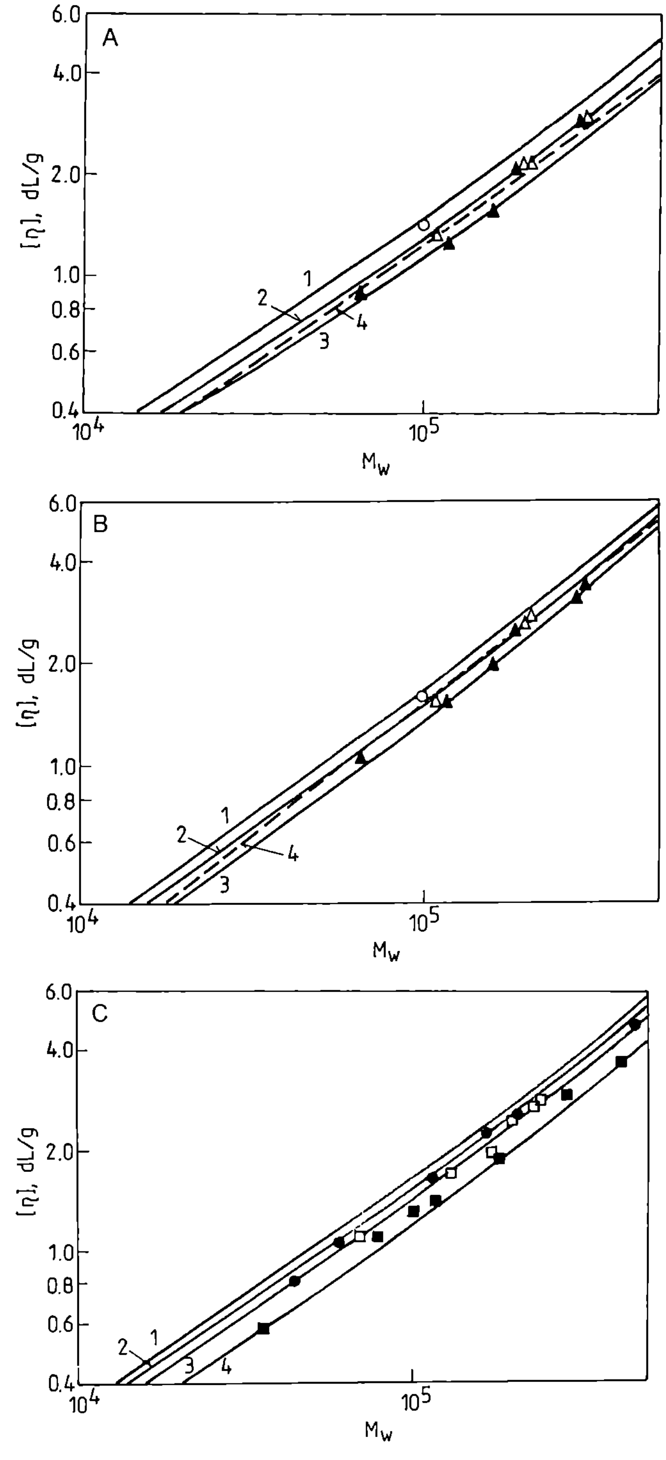

Fig. 3. The relationship [η] vs. M_w for EPM at 130°C: (a) TCB, (b) decalin; solid curves calculated by eqn. (3) and $\Delta B_{AB} = 0$ for $x_B = 0.2$, 0.4 and 0.6. Dashed curves calculated by eqn. (1) and parameters from Ref. [3] (see text); experimental points [11]: $x_B < 0.1$ (○), 0.2—0.4 (△), 0.48—0.6 (▲); (c) tetralin; curves 1—4 calculated with eqn. (3) and $\Delta B_{AB} = 0$ for $x_B = 0.2$, 0.3, 0.4, and 0.6; experimental points for $x_B = 0.28$ (□) [12], 0.25 (■) and 0.5 (•) [2], resp.; x_2 — mole fraction of propylene units

ships refer to EPM copolymers — some samples used for checking purposes were EPDM terpolymers with low diene contents. A small amount of these units does not affect the solution properties unless they produce long chain branching.

Data for trichlorobenzene and decalin have been reported by Scholte *et al.* [11]. We have divided them into three groups with $w_P < 0.1$, 0.2—0.45, and 0.45—0.6. Those of the second and third groups adhere well to the calculated curves (Fig. 3 a, b). With EPM in tetralin (Fig. 3c), the experimental and the calculated data dependences at $0.3 < w_P < 0.6$ are quite consistent. The effect of composition is clearly seen.

The dashed lines Figs. 3 a, b were calculated by means of eqn. (1) with values of K and a reported by Ver Strate [3] for EPDM copolymers with $x_P = 0.4$ to 0.5 (*i.e.*, $K = 2.74 \cdot 10^{-4}$ and $a = 0.759$ for decalin at 130°C; and $K = 2.92 \cdot 10^{-4}$ and $a = 0.726$ for trichlorobenzene at 135°C). The line for trichlorobenzene is situated between the theoretical lines for $x_P = 0.4$ and 0.5, and the line for decalin is very close to the theoretical line for $x_P = 0.4$. The agreement is good.

Universal calibration of SEC for polyolefines

The calibration of SEC and evaluation of data is based on the following assumptions [4]:

(*i*) The retention volume V_e is related to polymer chain dimensions, *e.g.*, to the mean-square end-to-end distance $<R^2>$. In a good solvent system, where the mean-square end-to-end distance is higher than in the unperturbed state $<R^2>_0$, it is the related to the molecular weight by the equation:

$$<R^2> = (<R^2>_0 /M)_\infty \cdot M \cdot \alpha_R^2 \tag{15}$$

where *the expansion factor* α_R^2 *is a function of the excluded-volume variable* z which is defined as [12]

$$z = 0.33\,\Phi_{0,\infty}(B/K_0)\cdot M^{1/2} \tag{16}$$

(*ii*) There exists a simple relationship between $<R^2>$ and the hydrodynamic volume [η] M

$$[\eta]M = \Phi <R^2>^{3/2} \tag{17}$$

(*iii*) According to the classical theory [38], the Flory viscosity coefficient Φ for random coils in the non-draining regime is a universal constant independent of the polymer molecular weight and polymer-solvent interactions. Thus, the viscosity expansion factor α_η^3 defined by eqn. (5) is assumed to be identical with α_R^3, so the logarithmic plot of [η] M *vs.* $<R^2>^{3/2}$ should be linear and universal and its slope should equal unity.

More recent theoretical and experimental studies have shown [12, 15, 39] that, at variance with the classical theory, Φ is not a universal *constant*. Except for the Θ state, where Φ is equal to $\Phi_{0,\infty}$ [*cf.* eqn. (4)], Φ decreases as z is increased, so the viscosity expansion factor α_η^3 is lower than α_R^3. We can write

$$p(z) = \alpha_\eta^3 / \alpha_R^3 = \Phi / \Phi_{0,\infty} < 1 \tag{18}$$

Consequently, the logarithmic plot of [η] M *vs.* $<R^2>^{3/2}$ is not universal (except in the Θ state) and its slope is lower than unity, the more so the higher the expansion factors or the variable z.

There is little agreement between theoretical functions p(z) and experimental results [15]. However, if based on the theories of the expansion factors [40, 41] the p (z) function fits, at least semiquantitatively, to the main features of the dependence of Φ on z. Therefore, it is most suitable for the discussion of the limits of the universal calibration. The equations [40, 41] are

$$\alpha_R^2 = (1+20z+155.54z^2+591.86z^2+325z^4+1670z^6)^{1/15} \tag{19}$$

$$\alpha_\eta^3 = (1+3.8z+1.9z^2)^{0.3} \tag{20}$$

Figure 4 presents the logarithmic plots of [η] *M vs. X*,

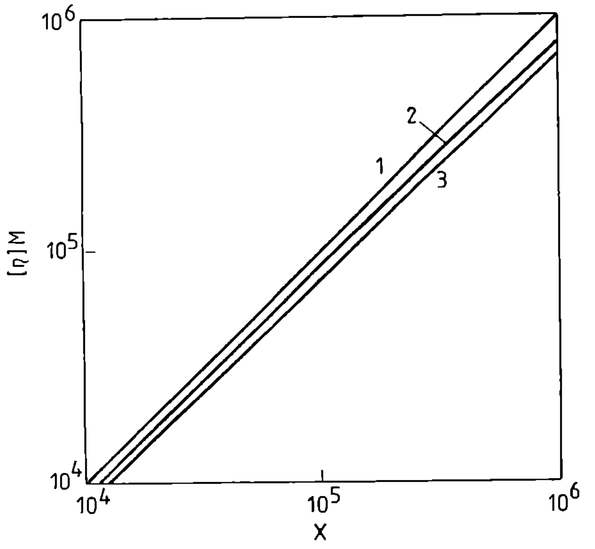

Fig. 4. Calculated relationship [η] M vs. X; X stands for $\Phi_{0,\infty} < R^2 >^{3/2}$*; curve 1 corresponds to the universal calibration; curves 2 and 3 for PE and PP (in TCB, 130°C) (for details, see text)*

where $X = \Phi_{0,\infty} < R^2 >^{3/2}$. Curve 1 corresponds to the universal calibration where $[\eta]\ M = \Phi_{0,\infty} <R^2>^{3/2}$. Curves 2 and 3 show the situation with PE and PP in TCB at 130°C. The z-values were calculated from of eqn. (16) by using K_0 (Fig. 1) and *B* (Table 1) and were substituted into eqns. (19) and (20). Deviations of curves 2 and 3 from curve 1 are seen to be significant and to increase as the molecular weight is increased. They amount to 10% and 20% with PE and to 15% and 30% with PP at $X = 10^4$ and 10^6, respectively. The curves for PE and PP are less different (<10% at $X = 10^4$, ~10% at $X = 10^6$).

The consequences for SEC calibration are illustrated with some calculated examples. For simplification, the values of [η] *M* and *X* were plotted against *M*. The molecules of PE (subscript 1) and PP (2), whose size is $X = 10^6$, are assumed to be eluted at a chosen retention volume. Their molecular weights are $M_1 = 250 \cdot 10^3$ and $M_2 = 410 \cdot 10^3$. The corresponding hydrodynamic volumes, $([\eta]\ M)_1 = 780 \cdot 10^3$ and $([\eta]\ M)_2 = 680 \cdot 10^3$, are lower than *X* and differ by about 15%.

1. We assume the column to have been calibrated against polypropylene (polymer 2) and we choose $([\eta]\ M)_2 = 680 \cdot 10^3$. According to the principle of the universal calibration, the value of $([\eta]\ M)_1$ of the polyethylene molecules eluted at the same retention volume should be equal to $([\eta]\ M)_2$, *i.e.*,

$$([\eta]\ M)_{1,UC} = ([\eta]\ M)_{2,UC} \tag{21}$$

The molecular weight of PE corresponding to this value, $M_{1^*} = 240 \cdot 10^3$, is lower than the correct value ($M_1 = 250 \cdot 10^3$) by less than 10%.

2. Let us assume that polyethylene has been used for calibration and choose $([\eta]\ M)_1 = 780 \cdot 10^3$. The corresponding molecular weight of PP estimated by using the universal calibration principle, eqn. (20), is $M_{2^*} = 440 \cdot 10^3$. In this case the "apparent" molecular weight M_{1^*} is higher than the true value by less than 10%.

3. In the third example, we assume that the calibration has been carried out by a Θ system (curve 1, Fig. 4) and that, as in the previous examples, $X = 10^6$. Assuming the universal calibration [eqn. (20)] to be valid, we find the $([\eta]\ M)_1$ value of PE to be 10^6.

The corresponding molecular weight, $M_{1^{**}} = 300 \cdot 10^3$, is higher than the correct value of M_1 by about 20%. For PP, we would obtain $M_{2^{**}} = 500 \cdot 10^3$, again higher by the same amount.

It may be concluded that, even if the assumption that $\alpha_\eta^3 = \alpha_R^3$ is not valid but the principle of the universal calibration is used, the molecular weights of polypropylene and polyethylene can be estimated by SEC with an accuracy that is the better the closer are the correlations of [η] *M vs. X* for the calibration of the polymers analyzed. These rules are also valid for EPM copolymers.

The B_{AB} parameter for PE and PP

Good agreement of the experimental data with the calculated molecular weight relationships of the intrinsic viscosity of EPM copolymers is shown to hold true with $\Delta B_{AB} \cong 0$. This means that B_{AB} is nearly equal to the arithmetic mean of the B_{AA} and B_{BB} values. We feel, however, that it is pertinent to examine the sensitivity of the *B* values for copolymers to the values of B_{AB} or χ_{AB} and to establish the conditions for a reliable estimation of these parameters.

By eqn. (14), the values of the solubility parameters mentioned above and $V_1 = 160$ mL/mol for α-chloronaphthalene give the enthalpic parameter as $\chi_{AB}^h = 0.067$. The χ-values for homopolymers calculated from the *B*-values in Table 1 are 0.23 and 0.41 for PE and PP, respectively. The values of $x_A x_B \chi_{AB}$ are plotted against x_A in Fig. 5. It is seen that the enthalpic term alone would raise the *B* parameter by less than 8% only. With regard to the accuracy of the *B* values, this increase is on the verge of significance. Using a higher χ_{AB} value, *e.g.*, 0.15, with a significant entropic contribution ($\chi_{AB}^s = 0.08$), we obtain a larger increase in B. It would be noticeable particularly at $x_A = 0.5$ where it amounts to 20%.

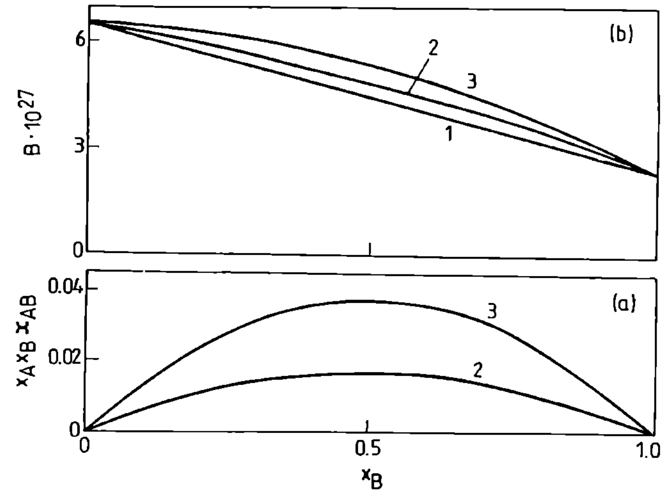

Fig. 5. (a) The calculated term $x_A x_B \chi AB$ and (b) the B-parameter vs. copolymer composition x_B — mole fraction of propylene units; curves 1 to 3 were calculated for EPM copolymers with eqn. (12) and $\chi_{AB} = 0$ (1), $\chi_{AB} = \chi^{h}_{AB} = 0.067$ (2) and $\chi_{AB} = 0.15$ (3) (details in text)

It can be seen that only large positive entropic contributions can raise the *B* parameter of EPM copolymers significantly. This condition would be less severe if the *B* parameters for homopolymers were low. This is illustrated by the following example. As follows from eqn. (12), optimum conditions would be attained with $x_A\chi_A + x_B\chi_B \cong 1/2$, *i.e.*, if the solvent were Θ-solvent for both homopolymers at identical or nearly identical temperatures. In such a case, the term $x_A x_B \chi_{AB}$ would be larger that the value of $[\frac{1}{2} - (x_A\chi_A + x_B\chi_B)]$. With EPM copolymers these conditions would best be met in diphenyl, where Θ (°C) = 127 [27] and 125.5 [30] for PE and PP, respectively, and somewhat worse in diphenyl ether, where Θ (°C) = 163.9 [30] and 142.8 [30] for PE and PP, respectively. Using these systems a reliable value of the χ_{AB} parameter could be obtained. We are aware of no measurements with EPM copolymers carried out at these temperatures.

ACKNOWLEDGMENT

The Authors wish to thank the Academy of Sciences of the Czech Republic for financial support (No. 12/96/K).

REFERENCES

1. Baldwin F. P., Ver Strate G.: *Rubber Chem. Technol.* 1972, **45**, 709.
2. Cesca S.: *J. Polym. Sci., Macromol. Rev.* 1975, **10**, 1.
3. Ver Strate G.: "Encyclopedia of Polymer Science and Engineering" (Mark H., Bikales N. M., Overberger G., Kroschwitz J. I., *Eds.*), J. Wiley, New York 1986, **6**, 522.
4. Benoit H., Grubisic Z., Rempp P., Decker D., Zilliox J. G.: *J. Chim. Phys.* 1966, **63**, 1607.
5. Wang K. Q., Zhang S. Y., Lu J., Li Ya.: *J. Liquid Chromat.* 1982, **5**, 1899.
6. Cinquina P., Gianotti G., Borghi D.: *Polymer* 1991, **32**, 2049.
7. Cinquina P., Gianotti G., Borghi D.: *Polymer Commun.* 1990, **31**, 30.
8. Smith W. V.: *J. Appl. Polym. Sci.* 1974, **18**, 3685.
9. Moraglio G.: *Chim. Ind.* (Milano) 1959, **10**, 984.
10. Crespi G., Valvassori A., Zamboni V., Flisi U.: *Chim. Ind.* (Milano) 1973, **55**, 130.
11. Scholte Th. G., Meijerink N. L. J., Schoffeleers H. M., Brands M. G.: *J. Appl. Polym. Sci.* 1984, **29**, 3763.
12. Yamakawa H.: "Modern Theory of Polymer Solutions". Harper and Row, New York 1971.
13. Stockmayer W. H., Moore L. D., Fixman M., Eps- tein B. N.: *J. Polym. Sci.* 1955, **16**, 517.
14. Fukuda T., Inagaki H.: *Pure Appl. Chem.* 1983, **55**, 1541.
15. Bohdanecký M., Kovář J.: "Viscosity of Polymer Solutions". Polymer Science Library (Jenkins A. J., *Ed.*), Elsevier, Amsterdam 1983.
16. Kotaka T., Tanaka T., Ohnuma H., Murakami Y., Inagaki H.: *Polymer J.* 1970, **1**, 242.
17. Arnett R. L., Stacy C. J.: *J. Phys. Chem.* 1986, **77**, 1973.
18. Staszewska D., Bohdanecký M., Huppenthal L.: *Polymer* 1992, **33**, 4878.
19. Van Krevelen D. W., Hoftyzer P. J.: "Properties of Polymers", Elsevier, Amsterdam 1972, 85.
20. Schreiber H. P., Waldman M. H.: *J. Polym. Sci. Part A* 1964, **2**, 1655.
21. Chiang R.: *J. Phys. Chem.* 1965, **69**, 1645.
22. Hama T., Yamaguchi K., Suzuki T.: *Makromol. Chem.* 1974, **155**, 283.
23. Wagner H. L., Hoeve C. A.: *J. Polym. Sci., Polym. Phys. Ed.* 1973, **11**, 1189.
24. Yamaguchi K.: *Makromol. Chem.* 1958, **128**, 19.
25. Chiang R.: *J. Polym. Sci.* 1958, **28**, 235.
26. Kinsinger L. B., Hughes B. E.: *J. Phys. Chem.* 1959, **63**, 2002; 1963, **67**, 1922.
27. Parini P., Sebastiano F., Messina G.: *Makromol. Chem.* 1960, **38**, 27.
28. Wagner H. L., Hoeve C. A. J.: *J. Polym. Sci., Polymer Symp.* 1976, **54**, 327.
29. Wagner H. L., Hoeve C. A. J.: *J. Polym. Sci., Polym. Phys. Ed.* 1976, **19**, 289.
30. Nakajima H., Hamada F., Hayaschi S.: *J. Polym. Sci. Part C* 1961, **15**, 286.
31. Helmstedt M., Bohdanecký M., Stejskal J.: *Polymer* 2001, **42**, 4163.
32. Flory P. J.: "Statistical Mechanics of Chain Molecules". Interscience, New York 1969.
33. Kinsinger J. B., Hughes R. E.: *J. Phys. Chem.* 1963, **67**, 1922.
34. Mays J. W., Fetters L. J.: *Macromolecules* 1989, **22**, 921.
35. Mays J. W., Hadjichristidis N., Fetters L. J.: *Macromolecules* 1984, **17**, 2723.
36. Xu Z., Mays J. W., Chen X., Hadjichristidis N., Schilling F. C., Bair H. E., Pearson D., Fetters L. J.: *Macromolecules* 1985, **18**, 2560.
37. Bohdanecký M., Sikora A., Horský J., Petrus V.: *Collect. Czech. Chem. Commun.* 1995, **60**, 1950.
38. Flory P. J.: "Principles of Polymer Chemistry". Cornell University Press, Ithaca 1953.
39. Fujita H.: "Polymer Solutions". Elsevier, Amsterdam 1990.
40. Lax M., Barrett A. J., Domb C.: *J. Phys. A., Math. Gen.* 1978, **11**, 361.
41. Barrett A. J.: *Macromolecules* 1984, **17**, 1561.