

Polymers in mixed solvents: linear representation of viscosity data as a function of molecular weight

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In this paper the corrected Stockmayer–Fixman–Burchard equation recently proposed¹³ is applied to the case of polymers dissolved in mixed solvents. A linear plot for viscosity over a very broad range of molecular weights is observed. The unperturbed dimensions of polymers obtained in mixed solvents are related to the thermodynamic properties of the solvent mixtures.

INTRODUCTION

The Stockmayer–Fixman–Burchard equation^{1,2} has often been used to correlate the intrinsic viscosity of a polymer with its molecular weight when it is dissolved in a binary mixture of solvents. The same equation has also been used to determine the unperturbed dimensions of a polymer in mixed solvents and it has always been observed that they are larger or smaller than those determined for the same polymer in a θ solvent or more generally in pure solvents^{3–12}.

The purpose of this article is to show that the equation recently proposed¹³, which gives a linear correlation between the viscosity of a polymer in a pure solvent and its molecular weight, over a very wide range, can also be applied when the polymers are dissolved in mixtures of solvents.

The ternary systems (1 polymer–2 solvents) investigated in this work exhibit a low preferential solvation of the polymer which for two of them does not change with molecular weight. It will be shown that it is possible in these special cases to determine the correct unperturbed dimensions of the polymers by extrapolation to zero molecular weight.

EQUATIONS

The variation of intrinsic viscosity $[\eta]$ as a function of the molecular weight of the polymers in mixed solvents will be represented by the three following equations:

Mark–Houwink equation

$$[\eta] = KM^a \quad (1)$$

Stockmayer–Fixman–Burchard equation (refs 1 and 2)

$$[\eta]/M^{1/2} = K_\theta + 0.51\phi_0 BM^{1/2} \quad (2)$$

Equation proposed in ref 13

$$[\eta]/M^{1/2} = \frac{1}{A_1} + \left(\frac{A_2}{A_1^2} \right) M^{1/2}(1 - DM^{1/2}) \quad (3)$$

In the above equations, the a , B , A_2 and D parameters represent the interactions between the polymer and the solvent

(or the mixture of solvents). The K_θ and A_1 parameters represent the unperturbed dimensions of the polymer and fit the two equations:

$$K_\theta = \frac{[\eta]_\theta}{M^{1/2}} \quad (4)$$

and according to ref 14:

$$\frac{1}{A_1} = \frac{K_\theta}{(1 - K_\theta A') } \quad (5)$$

In equation (5), the A' parameter is determined from the equation:

$$-\Delta\rho = -\Delta\rho_\infty + \frac{A'}{M^{1/2}} \quad (6)$$

$\Delta\rho$ represents the difference between the segment density of the polymer in solution in a given solvent and its density in segments at the θ conditions and is obtained through the relation^{14,15}:

$$\Delta\rho = \rho - \rho_\theta \sim \frac{1}{[\eta]} - \frac{1}{[\eta]_\theta} \quad (7)$$

The D parameter is related to the a exponent of the Mark–Houwink equation by the relation¹³:

$$D = 12 \times 10^{-4} (a - 0.5) \quad (8)$$

RESULTS

Some of the viscometric results presented here have been taken either from the literature or from our own articles. Our new results have been obtained using a FICA automatic viscometer. The values of the intrinsic viscosity will be expressed in cm^3/g . The molecular weights of the polymer samples have been determined using a FICA photogoniometer. The polydispersity of our samples as determined by gel permeation chromatography is always

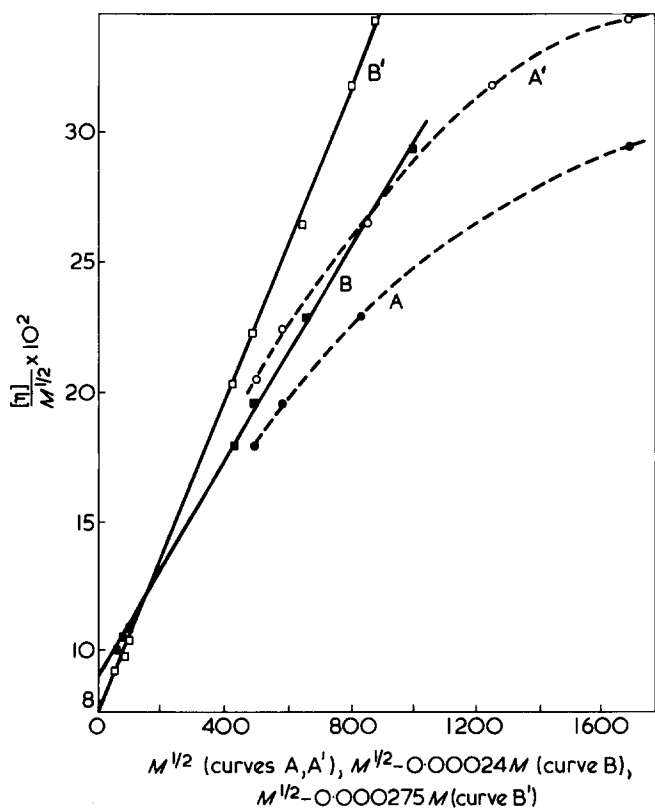


Figure 1 Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ for PS samples in benzene at 30°C (curve A') and in 50% benzene-50% cyclohexane at 30°C (curve A). $[\eta]/M^{1/2}$ versus $M^{1/2}$ -DM for the same PS samples: in benzene with $D = 0.000275$ (curve B'); in 50% benzene-50% cyclohexane with $D = 0.00024$ (curve B)

low. The composition of the mixtures of solvents is expressed in vol %.

The first system studied is polystyrene-50% benzene-50% cyclohexane at 30°C. The values of $[\eta]$ for the higher molecular weight samples have been taken from the paper of Yamakawa *et al.*¹⁶. We have determined the value of $[\eta]$ on three PS samples of low molecular weight. In Figure 1 we have plotted the variation of $[\eta]$ as a function of the molecular weight of the polymer according to equation (2) (curve A) and according to equation (3) (curve B). The value of D ($D = 0.00024$) is obtained from equation (8) since when $\log [\eta]$ is plotted as a function of $\log M$ a value $a = 0.7$ is obtained.

The preferential solvation of PS by benzene in a 50% benzene-50% cyclohexane mixture is low when the molecular weight of the polymer exceeds 100 000¹⁷.

In Figure 1 we have also represented for comparison, the variation of $[\eta]$ as a function of M using equations (2) and (3) (curves A' and B') for polystyrene in pure benzene solution at 30°C. It is seen that the two straight lines B and B' intersect producing an inversion of the viscosity. In other words the intrinsic viscosity of low molecular weight samples is higher in the mixed solvent than in pure benzene. This could be explained by the fact that unperturbed dimensions play a more important role in determining the $[\eta]$ value of a polymer when its molecular weight is very low than when the molecular weight is high.

The second ternary system investigated consists of polystyrene-85% cyclohexane-15% ethanol at 25°C. This solvent mixture is actually a cosolvent system of the polymer. This system has been studied particularly because the polymer does not exhibit any variation of preferential solvation

with molecular weight: this means that in a 85% cyclohexane-15% ethanol mixture we can observe an 'isoshestic' point for the preferential solvation of the polymer¹⁸.

In this system, the polystyrene is below the θ conditions. Plotting $\log [\eta]$ as a function of $\log M$, one obtains $a = 0.42$ and from equation (8), $D = -0.0001$. The straight line in Figure 2 gives the variation of $[\eta]$ as a function of the molecular weight according to equation (3). The use of equation (2) for this system yields an almost identical curve since we are very close to the θ conditions (low value of D) and since one cannot use high molecular weight polymers (precipitation).

The third system studied is poly(2-vinylpyridine)-80% CHCl_3 -20% ethanol at 25°C. The values of $[\eta]$ are taken from one of our former papers⁶ and have been complemented by additional measurements especially for low molecular weight samples.

When $\log [\eta]$ is plotted as a function of $\log M$, $a = 0.78$ is obtained without taking into account the values of $[\eta]$ corresponding to molecular weights below 70 000 (Figure 3). From equation (8), $D = 0.000336$ (calculated) and using equation (3) the straight line, B, in Figure 4 is ob-

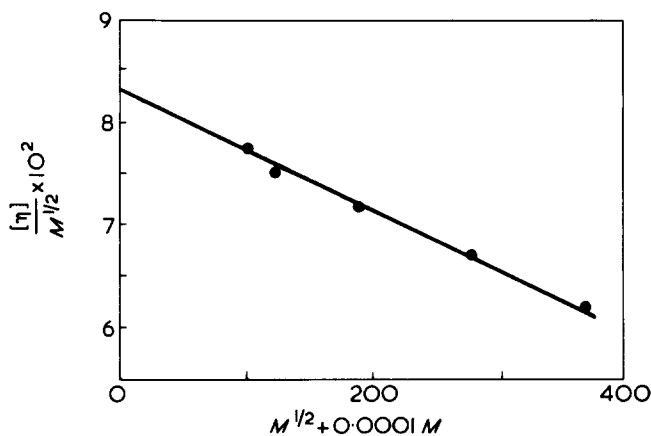


Figure 2 Plot of $[\eta]/M^{1/2}$ versus $M^{1/2} + 0.0001M$ for PS samples in 85% cyclohexane-15% ethanol at 25°C

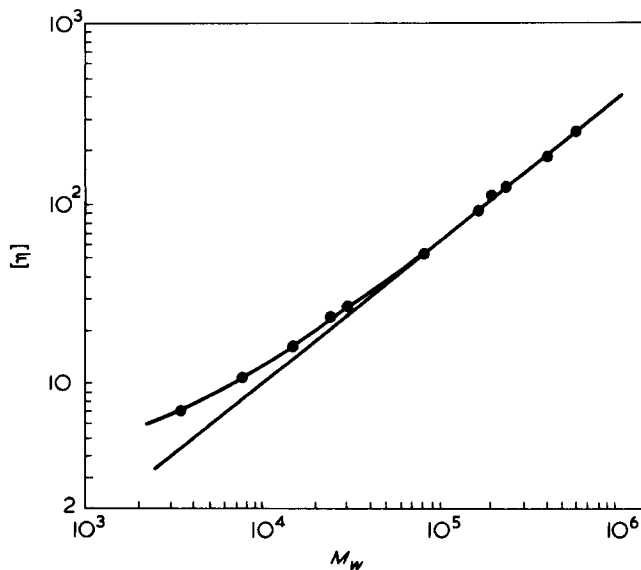


Figure 3 Plot of $\log [\eta]$ versus $\log M$ for poly(2-vinyl pyridine) samples in 80% CHCl_3 -20% ethanol at 25°C

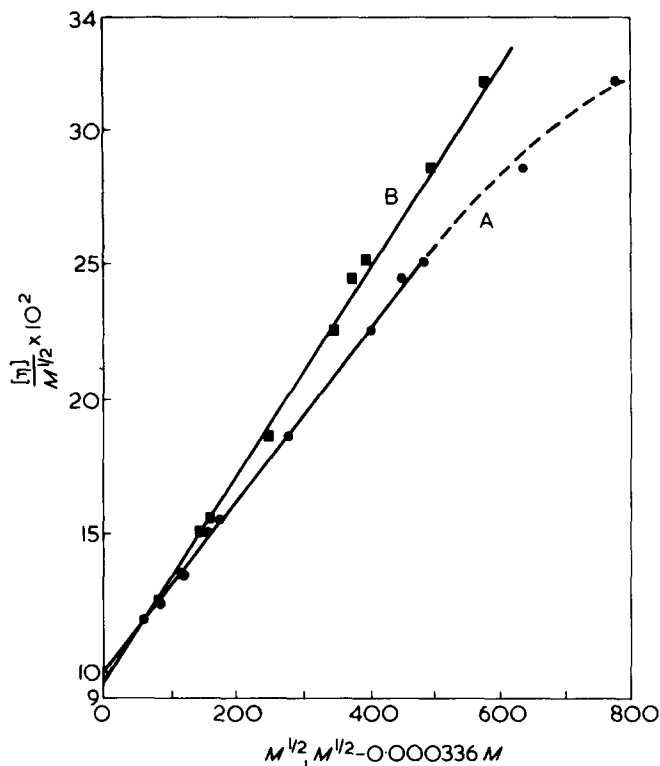


Figure 4 Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ (curve A) and versus $M^{1/2} - 0.000336 M$ (curve B) for poly(2-vinyl pyridine) samples in 80% CHCl_3 -20% ethanol at 25°C

tained. Curve A in the same Figure represents our viscometric results according to equation (2). A good linear relationship is obtained only from using equation (3). Equation (1) produces a deviation for low molecular weight samples (Figure 3) and equation (2) produces a deviation for higher molecular weight samples (Figure 4).

The final system studied is PMMA-82.5% CCl_4 -17.5% methanol at 25°C. Katime and Strazielle¹⁹ have shown that PMMA exhibits a very low preferential solvation in this mixture of solvents and that it does not change with the molecular weight of the polymer. The CCl_4 -methanol mixture is a cosolvent mixture for PMMA.

Plotting $\log [\eta]$ as a function of $\log M$ (values from Table 1) one obtains $a = 0.7$ and from equation (8), $D = 0.00024$. In Figure 5, curve A is obtained from equation (2) and the straight line B from equation (3). Also, equation (3) yields a better linearity between $[\eta]$ and M over a wide range of molecular weight.

DISCUSSION

It is seen in Figures 1, 2, 4 and 5 that the equation that we have proposed¹³ (equation 3) applies well to the viscometric results obtained with polymers dissolved in mixed solvents. Moreover, the relation between a and D (equation 8) that we have established for polymers dissolved in pure solvents applies also for polymers dissolved in mixed solvents.

The simple equation¹⁴:

$$\frac{1}{[\eta]} = -A_2 + \frac{A_1}{M^{1/2}} \quad (9)$$

which can be used in the low and medium ranges of molecular weight has been applied to cases where polymers are

dissolved in mixed solvents²⁰. In Figure 6 we show the application of equation (9) for two systems studied in this work. In the case of the system PMMA-82.5% CCl_4 -17.5% methanol it is valid for molecular weights up to about 300 000. The finding of a positive value for $-A_2$ in the PS-85% cyclohexane-15% ethanol system means that in this case, the PS is below θ conditions.

As we have already noted, in the systems presented in this paper we find a low preferential solvation of the polymer. This solvation is completely independent of the molecular weight for the two systems^{18,19}: PS-85% cyclohexane-15% ethanol, and PMMA-82.5% CCl_4 -17.5% methanol. We can then claim that the extrapolation to zero molecular weight of the linear part of the curves obtained through equation (2) is justified and that it gives the unperturbed dimensions of the polymers.

The K_θ values of the polymers, obtained in the solvent mixtures studied are higher than those determined when the polymers are in solution in a θ solvent. For PMMA in *p*-xylene (θ solvent) we have obtained²¹ $K_\theta = 5 \times 10^{-2}$, whereas in the mixture CCl_4 -methanol we obtain $K_\theta = 7.4 \times 10^{-2}$ (Figure 5). The value of K_θ of a polymer dissolved in a mixture of solvents, is also higher than the value calculated from the K_θ values corresponding to the same polymer dissolved in each of the pure solvents. As an example we present poly(2-vinyl pyridine) which has a K_θ value equal to 10×10^{-2} in the mixture 80% CHCl_3 -20% ethanol (Figure 4) whereas we obtain, for the same polymer in pure ethanol $K_\theta = 8.3 \times 10^{-2}$ and in pure CHCl_3 $K_\theta = 8.7 \times 10^{-2}$.

We have attributed the increase of the K_θ values in mixed solvents to the positive value of the excess free enthalpy of mixing of the solvents ΔG^E . Thus one observes

Table 1 Intrinsic viscosity values for PMMA samples in 82.5% CCl_4 /17.5% methanol solvent mixture at 25°C

$M_w \times 10^{-3}$	$[\eta]$ (cm ³ /g)	$M_w \times 10^{-3}$	$[\eta]$ (cm ³ /g)
10	8.6	550	110
13	10.0	1040	178
22	13.0	1277	210
65	26.8	1300	199
88	31.5	2400	310
115	38.5	3100	360
160	49.0	5760	490
280	71.5		

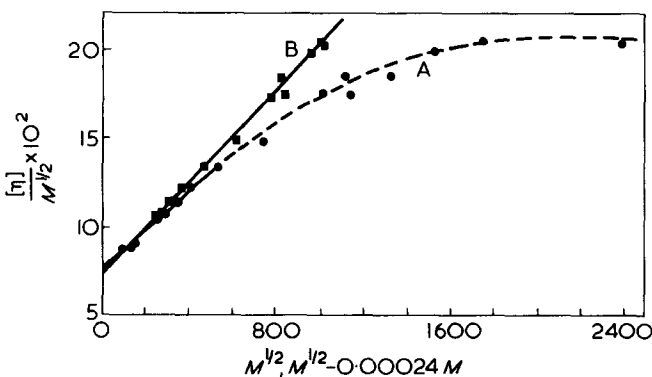


Figure 5 Plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ (curve A) and versus $M^{1/2} - 0.00024 M$ (curve B) for PMMA samples in 82.5% CCl_4 -17.5% methanol at 25°C

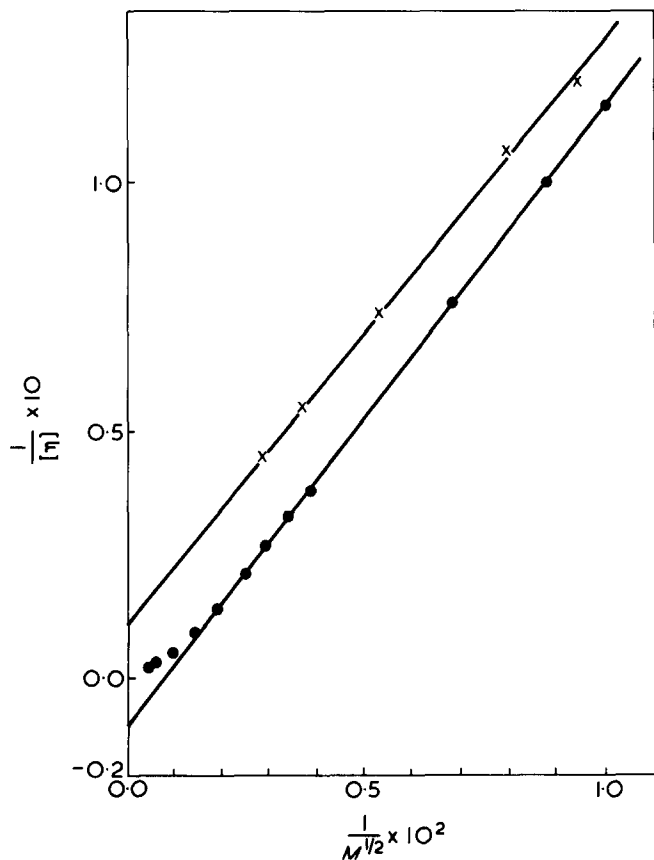


Figure 6 Plot of $1/[\eta]$ versus $1/M^{1/2}$. X, PS samples in 85% cyclohexane–15% ethanol at 25°C; ●, PMMA samples in 82.5% CCl_4 –17.5% methanol at 25°C

that in the four mixtures of solvents used here, different authors have obtained positive ΔG^E values^{22–25}.

Although we have found a very good linear relationship between $[\eta]/M^{1/2}$ and $M^{1/2}$ – DM using equation (3) for a wide range of molecular weights this equation does not enable us to determine directly the unperturbed dimensions of the polymers. Indeed, in order to obtain K_θ values from $1/A_1$ values using equation (5) we have to determine A' . In order to determine the A' value through equations (6) and (7) it is necessary to know the K_θ value. Nevertheless since A' is always small it can be neglected and we can consider that K_θ is equal to $1/A_1$.

In conclusion we will now discuss the results of Pouchly and Patterson²⁶ according to whom the K_θ value obtained through the Stockmayer–Fixman–Burchard equation depends on long range interactions, particularly when polymers are dissolved in mixed solvents. According to these authors the value obtained by extrapolating to zero molecular weight the straight line obtained from a $[\eta]/M^{1/2}$ versus $M^{1/2}$ plot is not equal to K_θ but to $(1 + B_2)K_\theta$. They have used Flory and Orofino's calculation and have obtained:

$$\alpha^3 - 1 = B_1 M^{1/2} + B_2 \quad (10)$$

which gives:

$$[\eta]/M^{1/2} = (1 + B_2)K_\theta + B_1 K_\theta M^{1/2} \quad (11)$$

instead of equation (2).

Then, comparison of equations (2) and (11) gives:

$$B_1 = 0.51 B K_\theta^{-1} \phi_0 \quad (12)$$

For a polymer in a good solvent, B is of the order 2×10^{-27} and since $K_\theta \approx 8 \times 10^{-2}$ and $\phi_0 = 2.8 \times 10^{23}$, we obtain $B_1 \approx 0.004$ from equation (12). Since B_1 and B_2 are related to ξ_1 and ξ_2 from Flory–Orofino's paper^{26,27} and since generally, $\xi_2 < \xi_1$ it follows that $B_2 < B_1$. The value of B_2 that we obtain should therefore be smaller than 0.004 which leads to an insignificant correction factor for K_θ . This is in agreement with the results of Eskin *et al.*²⁸ Finally we give the PS–benzene system as evidence for the validity of K_θ obtained from equation (2).

For the PS–benzene system Candau, Strazielle and Benoit²⁹ have obtained a χ' value almost equal to zero and according to Pouchly and Patterson we should obtain by extrapolation a very different K_θ value from that obtained for PS in cyclohexane, where $\chi' \approx 1/3$. To our knowledge, the same value of K_θ for PS is always obtained in the two solvents.

REFERENCES

- 1 Stockmayer, H. W. and Fixman, F. *J. Polym. Sci. (C)* 1963, 1, 137
- 2 Burchard, W. *Makromol. Chem.* 1961, 50, 20
- 3 Dondos, A. and Benoit, H. *Macromolecules* 1973, 6, 242
- 4 Dondos, A. and Benoit, H. *Eur. Polym. J.* 1968, 4, 561
- 5 Dondos, A., Rempp, P. and Benoit, H. *J. Polym. Sci. (C)* 1970, 30, 9
- 6 Dondos, A. and Benoit, H. *Eur. Polym. J.* 1970, 6, 1439
- 7 Dondos, A. and Benoit, H. *Macromolecules* 1971, 4, 279
- 8 Tuzar, Z., Keltečková, J. and Králíček, J. *Collect. Czech. Chem. Commun.* 1974, 39, 2206
- 9 Gevorkyan, A. V. and Simonyan, L. Kh. *Vysokomol. Soedin. (A)* 1975, 17, 1922
- 10 Katime, I., Garro, P. and Teijon, M. *J. Eur. Polym. J.* 1975, 11, 881
- 11 Gargallo, L. *Colloid Polym. Sci.* 1975, 253, 288
- 12 Vira, F., Viras, K., Aroni, F. and Dondos, A. *Eur. Polym. J.* 1974, 10, 891
- 13 Dondos, A. and Benoit, H. *Polymer* 1978, 19, 523
- 14 Dondos, A. and Benoit, H. *Polymer* 1977, 18, 1161
- 15 Dondos, A. *Eur. Polym. J.* 1977, 13, 829
- 16 Takashima, K., Nakae, K., Shibata, M. and Yamakawa, H. *Macromolecules* 1974, 7, 641
- 17 Dondos, A. and Benoit, H. *Makromol. Chem.* 1978, 179, 1051
- 18 Dondos, A. *Makromol. Chem.* 1977, 178, 2421
- 19 Katime, I. and Strazielle, C. *Makromol. Chem.* 1977, 178, 2295
- 20 Dondos, A. *Polymer* 1977, 18, 1250
- 21 Dondos, A. and Benoit, H. *Makromol. Chem.* 1968, 118, 165
- 22 Scatchard, G., Wood, S. E. and Mochel, J. M. *J. Phys. Chem.* 1939, 43, 119
- 23 Scatchard, G. and Satkiewicz, F. G. *J. Am. Chem. Soc.* 1964, 86, 130
- 24 Barker, J. A. and Smith, F. J. *J. Chem. Phys.* 1954, 22, 375
- 25 Scatchard, G. and Ticknor, L. B. *J. Am. Chem. Soc.* 1952, 74, 3724
- 26 Pouchly, J. and Patterson, D. *Macromolecules* 1973, 6, 465
- 27 Orofino, T. A. and Flory, P. J. *J. Chem. Phys.* 1957, 26, 1067
- 28 Eskin, V. E., Nekrasova, T. N. and Juraev, U. *Eur. Polym. J.* 1975, 11, 341
- 29 Candau, F., Strazielle, C. and Benoit, H. *Eur. Polym. J.* 1976, 12, 95