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Determination of the exchange enthalpy and entropy parameters of the equation-of-state theory for poly(dimethyl siloxane) in various solvents

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The interaction parameter χ_t^∞ and the effective exchange energy parameter $\bar{X}_{12}$ at infinite dilution of cyclohexane, benzene and chlorobenzene with poly(dimethyl siloxane) were determined around room temperature, according to relations given in the Flory formulation of the equation-of-state theory using the inverse gas chromatography technique. Then, the exchange enthalpy X_{12} and entropy Q_{12} parameters were determined by using a relation for the enthalpy interaction parameter χ_h of the equation-of-state theory, which is arranged for the inverse gas chromatography conditions. The values of the above-mentioned parameters are comparable with the values obtained earlier with other methods. The X_{12} and Q_{12} parameters of cyclohexane increase slightly with temperature, while those of benzene and chlorobenzene are almost independent of temperature. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(dimethyl siloxane); polymer–solvent interactions; equation-of-state parameters)

INTRODUCTION

The equation-of-state theory introduced by Flory and coworkers during the 1960s[1–3] used some reduced parameters evaluated from the density, thermal expansion coefficient and thermal pressure coefficient of the pure components as well as an exchange enthalpy parameter X_{12} and an exchange entropy parameter Q_{12}, which depend on the difference in the chemical nature of the components. The X_{12} parameter is often obtained by fitting the theoretical equation for the experimental heats of mixing of analogous materials or experimental volume changes on mixing of the lower-molecular-weight polymer with solvents[4–8]. X_{12} is assumed to be independent of temperature, but this situation is not confirmed yet. Q_{12} can be adjusted for a particular system so as to have an agreement between a calculated quantity and an observed property under one set of conditions.

Recently, we proposed a direct procedure to obtain both X_{12} and Q_{12} by intrinsic viscosity measurements[9]. We continue to explore this procedure using several polymer–solvent systems[10–12].

In this study, we have determined X_{12} and Q_{12} directly from inverse gas chromatography (i.g.c.) measurements, which is an easy, fast, reliable and economical technique[13–15]. Another advantage of the i.g.c. technique is the possibility of working with both solvent and non-solvent of the polymer under the same experimental conditions.

We preferred the polymer–solvent systems studied before extensively[4,5,8], such as cyclohexane (CH), benzene (B) and chlorobenzene (CB) with poly(dimethyl siloxane) (PDMS), in order to check the accuracy of the method. In addition, all the equation-of-state parameters of CH, B, CB and PDMS were determined with a high precision. Therefore, errors that might arise from inaccurately estimated equation-of-state parameters were eliminated. Also, the glass transition temperature T_g of PDMS is very low (−42°C). The low T_g allows one to perform experiments around room temperature, since the i.g.c. method gives meaningful solubility results at temperatures at least 40°C higher than T_g. So, we avoided as much as possible errors coming through the extrapolation to room temperature of the values at high temperatures.

DATA REDUCTION

In the equation-of-state theory, Flory and coworkers have defined a different interaction parameter χ from the one in the Flory–Huggins theory. In this definition, molar volumes are replaced by the molar hard-core volumes and the segment fraction of polymer is used instead of its volume fraction. We denote the interaction parameter defined in the equation-of-state theory with the symbol χ_t^∞. The reason for the superscript ∞ is that the polymer concentration is very high since a trace amount of solvent is used for i.g.c. measurements. Therefore the χ_t^∞ parameter obtained by i.g.c. quantifies the interaction between polymer and solvent at infinite dilution of the solvent in the polymer; χ_t^∞ is obtained

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from i.g.c. measurements by the following equation:

$$\chi_t^{\infty} = \ln\left(\frac{273.2Rv_2^*}{p_1^{\circ} V_g^{\circ} V_1^*}\right) - \left(1 - \frac{V_1^*}{M_2 v_2^*}\right) - \frac{p_1^{\circ}(B_{11} - V_1)}{RT} \tag{1}$$

where R is the universal gas constant; T is the absolute column temperature; p_1°, V_1, V_1^* and B_{11} are the saturated vapour pressure, liquid molar and hard-core volume and second virial coefficient of the solvent, respectively; v_2^* and M_2 are the specific hard-core volume and molecular weight of the polymer, respectively; and V_g° is the specific retention volume obtained from i.g.c. experiments for the polymer–solvent pair.

In the Flory formulation of the equation-of-state theory, the value of χ_t^{∞} for infinitely dilute solution of the solvent is given by:

$$RT\chi_t^{\infty} = p_1^* V_1^* \left[3\tilde{T}_1 \ln\left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1}\right) + (\tilde{v}_1^{-1} - \tilde{v}_2^{-1})\right] + \frac{\bar{X}_{12}}{p_1^* \tilde{v}_2} \tag{2}$$

where $\tilde{v}$ and $\tilde{T}$ are reduced volume and temperature, and subscripts 1 and 2 are used to indicate solvent and polymer, respectively. They are calculated by using the following equations from the thermal expansion coefficients (α) of the pure components:

$$\tilde{v}^{1/3} = (V/V^*)^{1/3} = [(\alpha T/3)/(1 + \alpha T)] + 1 \tag{3}$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{4}$$

$$\alpha = (1/V)(\partial V/\partial T)_{p=0} \tag{5}$$

Here p_1^* is the characteristic pressure of the solvent and is calculated by means of the thermal pressure coefficient (γ) of the pure component:

$$p^* = \gamma T \tilde{v}^2 \tag{6}$$

$$\gamma = (\partial p/\partial T)_v \tag{7}$$

The $\bar{X}_{12}$ parameter in equation (2) is the effective exchange interaction parameter, which quantifies the change in contact energy when a polymer segment in the vicinity of another polymer segment is replaced by a solvent molecule. The $\bar{X}_{12}$ parameter combines the exchange enthalpy X_{12} and entropy Q_{12} parameters in the gas chromatographic conditions by the relation:

$$\bar{X}_{12} = X_{12} + \tilde{v}_2 T Q_{12} \tag{8}$$

On the other hand, the enthalpy interaction parameter χ_h is expressed according to equation-of-state theory by:

$$\chi_h = \frac{p_1^* V_1^*}{RT\Phi_2^2}\left(\tilde{v}_1^{-1} - \tilde{v}^{-1} + \frac{\alpha T(\tilde{T}_1 - \tilde{T})}{\tilde{v}\tilde{T}}\right) + \frac{V_1^*(1 + \alpha T)X_{12}\theta_2^2}{\tilde{v}RT\Phi_2^2} \tag{9}$$

where

$$\Phi_2 = m_2 v_2^*/(m_1 v_1^* + m_2 v_2^*) \qquad \Phi_1 = 1 - \Phi_2 \tag{10}$$

$$\theta_2 = (s_2/s_1)\Phi_2/[(s_2/s_1)\Phi_2 + \Phi_1] \qquad \theta_1 = 1 - \theta_2 \tag{11}$$

and Φ, θ and m are volume, segmental and weight fractions of a component in a mixture, respectively; symbols without an index denote mixture; and s_2/s_1 is the surface per unit of core volume ratio.

Equation (9) can be written for gas chromatographic conditions by replacing the equation-of-state parameters of the mixture with those of the polymer and $\Phi_1 = 0$ and $\Phi_2 = 1$. Then it is obtained that:

$$\chi_h^{\infty} = \frac{p_1^* V_1^*}{RT}\left(\tilde{v}_1^{-1} - \tilde{v}_2^{-1} + \frac{\alpha_2 T(\tilde{T}_1 - \tilde{T}_2)}{\tilde{v}_2 \tilde{T}_2}\right) + \frac{V_1^*(1 + \alpha_2 T)X_{12}}{\tilde{v}_2 RT} \tag{12}$$

χ_h^{∞} is related to χ_t^{∞} by the relation:

$$\chi_t^{\infty} = \chi_h^{\infty} + \chi_s^{\infty} \tag{13}$$

where χ_s^{∞} is the entropy interaction parameter at infinite dilution of solvent. The values of χ_h^{∞} are obtained by the equation[13–17]:

$$\chi_h^{\infty} = \Delta H_m^{\infty}/RT = [\partial(\chi_t^{\infty})/\partial(1/T)]/T \tag{14}$$

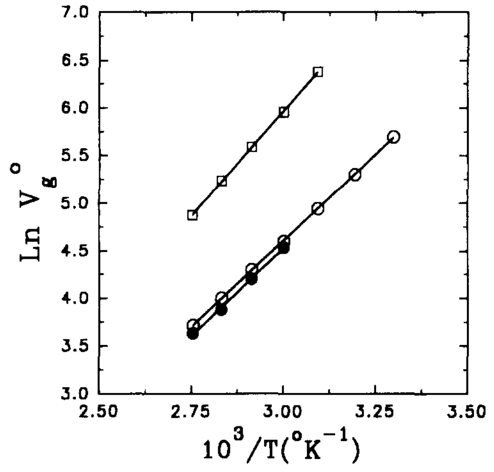

Figure 1 Variation of specific retention volume of the solvents with the reciprocal of absolute column temperature. Hollow circles belong to cyclohexane, filled circles to benzene and hollow squares to chlorobenzene

Table 1 Specific retention volume V_g°, interaction parameter χ_t^{∞} at infinite dilution of the solvent and effective exchange interaction parameter $\bar{X}_{12}$ of cyclohexane, benzene and chlorobenzene with poly(dimethyl siloxane) at various column temperatures

Solvents	Column temp. (°C)	V_g° (cm^3/g pol.)	χ_t^{∞}	$\bar{X}_{12}$ (J cm^{-3})
Cyclohexane	30	297.21	0.56	19.3
	40	199.99	0.55	19.0
	50	140.01	0.53	18.6
	60	99.52	0.52	18.4
	70	73.77	0.50	17.5
	80	54.65	0.50	17.6
	90	41.11	0.51	17.7
Benzene	60	93.26	0.75	34.6
	70	66.98	0.74	35.3
	80	48.47	0.75	36.6
	90	37.80	0.70	35.3
Chlorobenzene	50	589.21	0.94	37.8
	60	386.11	0.94	38.7
	70	266.81	0.91	38.5
	80	186.92	0.88	38.2
	90	130.70	0.88	39.2

Table 2 Comparison of the χ_t^∞ interaction parameter obtained in this study with literature values

Solvents	Temperature (°C)	χ_t^∞ (this study)	χ_t^∞ (literature)	Ref.
Cyclohexane	20	0.58[a]	0.58	19
	25	0.57[a]	0.47	20
	40	0.55	0.47	20
	70	0.50	0.48	20
	25	0.57[a]	0.60	5
	60	0.52	0.49	21
	80	0.50	0.50	21
	90	0.51	0.51[b]	21
Benzene	25	0.81[a]	0.79	20
	55	0.75	0.82	22
	70	0.74	0.81	22
	20	0.81[a]	0.85	22
	55	0.75	0.72	20
	70	0.74	0.71	20
	25	0.81[a]	0.86	23
	60	0.75	0.78	23
	80	0.75	0.75	21
Chlorobenzene	180	0.71[a]	0.7	24
	180	0.71[a]	0.68[c]	25

[a] Found by extrapolation of experimental data points to the indicated temperatures
[b] At 100°C
[c] The Flory–Huggins interaction parameter χ

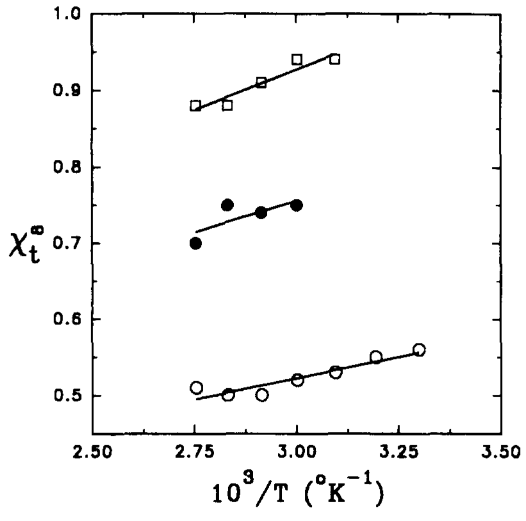

Figure 2 The interaction parameters χ_t^∞ of the solvents at infinite dilution with poly(dimethyl siloxane) as a function of reciprocal of the absolute column temperature. The solid lines are produced by first-order linear regression

In this equation ΔH_m^∞ is the enthalpy of mixing at infinite dilution of the solvent.

EXPERIMENTAL

Poly(dimethyl siloxane) was a Petrarch Inc. product with a number-average molecular weight of 2.8×10^4. Cyclohexane, benzene and chlorobenzene were analytical reagent grade and were used without further purification. The solvents and support material, viz. Chromosorb-W (AW-DMCS-treated, 80/100 mesh), were supplied by Merck AG. Inc. Silane-treated glass wool used to plug the ends of the column was obtained from Alltech Associates Inc.

A Hewlett-Packard 5890 model, series II gas chromatograph with a thermal conductivity detector was used in this study. The retention times of the solvents were recorded with a Yew 3201 model recorder. The flow rate of the carrier gas was kept below 6 cm^3 min^{-1}. Before the experiments, it was determined that the retention volume does not depend on the flow rate of the carrier gas below this flow rate.

The column was stainless-steel tubing with 3.2 mm o.d. and 1 m length. The preparation of the column material and injection of the solvents were given in the previous work[18]. The loading of the coated polymer on the support was determined as 7.24% by weighing the polymer, which was extacted from column material with benzene for 7 days.

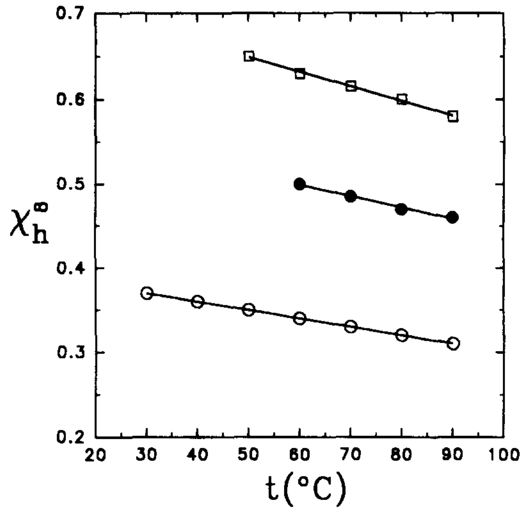

Figure 3 The enthalpy interaction parameters χ_h^∞ of the solvents at infinite dilution with poly(dimethyl siloxane) as a function of temperature

Table 3 Enthalpic interaction parameter χ_h^∞, entropic interaction parameter χ_s^∞, exchange enthalpy parameter X_{12} and exchange entropy parameter Q_{12} of cyclohexane, benzene and chlorobenzene with poly(dimethyl siloxane) at various column temperatures

Solvents	Column temperature (°C)	χ_h^∞	χ_s^∞	X_{12} (J cm^{-3})	Q_{12} (J cm^{-3} K^{-1})
Cyclohexane	30	0.37	0.19	11.2	-21.5
	40	0.36	0.19	11.5	-19.2
	50	0.35	0.18	11.5	-17.7
	60	0.34	0.18	12.0	-15.4
	70	0.33	0.17	12.6	-11.2
	80	0.32	0.18	12.4	-11.6
	90	0.31	0.20	13.2	-9.6
Benzene	60	0.50	0.25	19.3	-36.8
	70	0.48	0.26	19.0	-37.5
	80	0.47	0.28	19.0	-39.4
	90	0.46	0.24	18.7	-35.6
Chlorobenzene	50	0.65	0.29	20.5	-43.7
	60	0.63	0.31	20.5	-43.7
	70	0.61	0.30	20.9	-40.7
	80	0.60	0.28	21.1	-38.3
	90	0.58	0.30	20.6	-40.3

RESULTS AND DISCUSSION

The specific retention volume of the solvents obtained by inverse gas chromatography is plotted as a function of reciprocal of the absolute column temperature in *Figure 1*.

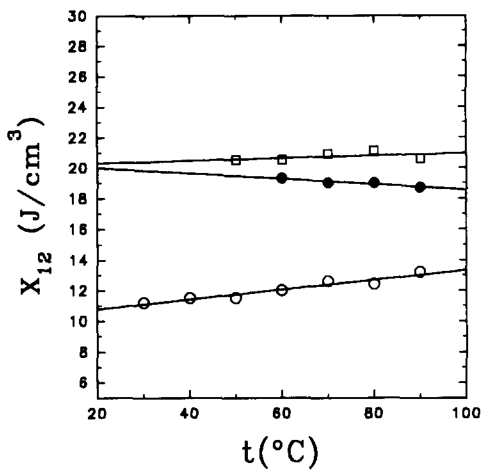

Figure 4 The exchange enthalpy parameters X_{12} of the solvents with poly(dimethyl siloxane) as a function of temperature

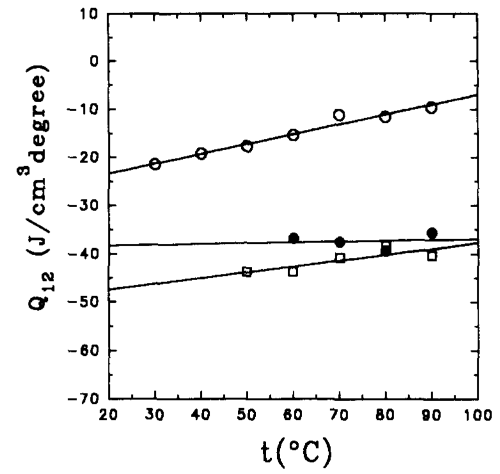

Figure 5 The exchange entropy parameters Q_{12} of the solvents with poly(dimethyl siloxane) as a function of temperature

The numerical data are given in *Table 1* together with interaction parameter χ_t^∞ and effective exchange energy parameter $\bar{X}_{12}$ obtained from equations (1) and (2). No peak was detected in the gas chromatography at temperatures lower than the indicated lowest temperatures. The data related to the reduced and characteristic parameters of the solvents and the polymer were taken from the literature[3,5,8].

In *Table 2*, the interaction parameter χ_t^∞ found in this study is compared with data found from the literature. Our data seem to have reasonable values since they are between the values given in the literature. Then, in *Figure 2*, the variation of χ_t^∞ with $1/T$ is plotted in order to obtain the values of χ_h^∞ according to equation (14). It was assumed that the values of χ_t^∞ vary linearly for the solvents and the temperature range studied in spite of scattering of the points. *Figure 3* exhibits the values of χ_h^∞ as a function of temperature. All of the values decrease with temperature.

The exchange enthalpy X_{12} and exchange entropy Q_{12} parameters, calculated by means of equations (8) and (10), as well as the χ_s^∞ values are collected in *Table 3*. *Figures 4* and *5* indicate the variation of X_{12} and Q_{12} with temperature, respectively. Although the values of both X_{12} and Q_{12} of B and CB are nearly independent of temperature, those of cyclohexane increase slowly with temperature.

In *Table 4*, we compare our X_{12} and Q_{12} values with previous work. The experimental techniques used in ref. 5 are osmotic pressure, vapour sorption and excess volumes of mixtures, while viscosity measurements are used in ref. 12. The data found for CH and B are comparable with the literature values, while X_{12} values of CB are far from the literature values, being rather close

Table 4 Comparison of the exchange enthalpy parameter X_{12} and exchange entropy parameter Q_{12} determined in this study with values found from literature

		This study		Ref. 5		Ref. 12	
Solv.	Temp. (°C)	X_{12} (J cm^{-3})	$Q_{12} \times 10^3$ (J cm^{-3} K^{-1})	X_{12} (J cm^{-3})	$Q_{12} \times 10^3$ (J cm^{-3} K^{-1})	X_{12} (J cm^{-3})	$Q_{12} \times 10^3$ (J cm^{-3} K^{-1})
CH	25	11	-25	8	-39		–
B	25	20	-42	22	-42	17	-39
CB	20	20	-48	11	-64		–
CB	60	20	-45	11	-59	–	–

Table 5 Comparison of the ΔH_m^∞ values found from equation (15) by using X_{12} and Q_{12} values obtained in this study and ref. 5 with the reported experimental values in the literature

		Expt.	This study		Ref. 5	
Solv.	Temp. (°C)	ΔH_m^∞ (J g^{-1})	s_1/s_2	ΔH_m^∞ (J g^{-1})	s_1/s_2	ΔH_m^∞ (J g^{-1})
CH	25	5.2[a]	1.7	5.2	1.2	5.2
B	25	14.2[a]	1.2	14.2	1.32	14.2
B	25	11.0[b]	1.5	11.1	–	–
CB	20	7.53[a]	2.0	8.7	1.4	6.8

[a] Ref. 25
[b] Ref. 26

to the values of benzene. This difference may appear from the values of s_1/s_2. In *Table 5*, our enthalpy of mixing $\Delta H_{\mathrm{m}}^{\infty}$ at infinite dilution of PDMS in solvents are compared with those found experimentally and those reported in ref. 5. The enthalpies of mixing were calculated by means of the equation:

$$\Delta \bar{H}_{\mathrm{m}}^{\infty} = (v_2^*/\tilde{v}_1)[X_{12}(s_2/s_1) + p_2^*(\tilde{v}_1/\tilde{v}_2 - 1) - \alpha_1 T p_1^* A \tag{15}$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (X_{12}/p_1^*)(s_2/s_1) \tag{16}$$

Suitable s_1/s_2 values were used to fit the enthalpy of mixing values obtained in this study and experimental ones. The required s_1/s_2 values are not very far from the s_1/s_2 values used in ref. 5.

In conclusion, it seems that X_{12} and Q_{12} parameters are composition-independent since X_{12} and Q_{12} parameters obtained in this study are comparable with those obtained at lower concentration range by other experimental techniques.

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REFERENCES

1 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507
2 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833
3 Abe, A. and Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1838
4 Shih, H. and Flory, P. J. *Macromolecules* 1972, **5**, 758
5 Flory, P. J. and Shih, H. *Macromolecules* 1972, **5**, 761
6 Flory, P. J. and Höcker, H. *Trans. Faraday Soc.* 1971, **67**, 2258
7 Höcker, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2270
8 Höcker, H., Shih, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2275
9 Yılmaz, F. and Baysal, B. M. *Polym. Int.* 1993, **3**, 107
10 Kuntman, A. and Baysal, B. M. *Polymer* 1993, **34**, 3723
11 Kuntman, A., Uyanık, N. and Baysal, B. M. *Polymer* 1994, **35**, 3356
12 Kuntman, A. and Yılmaz, F. *Polymer* 1995, **33**, 2107
13 Guillet, J. E. in 'New Developments in Gas Chromatography' (Ed. J. H. Purnell), Wiley-Interscience, New York, 1973, p. 187
14 Gray, D. G. in 'Progress in Polymer Science' (Ed. A. D. Jenkins), Vol. 5. Pergamon Press, Oxford, 1977, p. 1
15 Vilcu, R. and Leca, M. in 'Studies in Polymer Science', Elsevier, Amsterdam, 1990
16 Walsh, D. J. and Rostami, S. *Adv. Polym. Sci.* 1985, **70**, 119
17 Leung, Y.-K. *Polymer* 1976, **17**, 374
18 Yılmaz, F., Cankurtaran, Ö. G. and Baysal, B. M. *Polymer* 1992, **33**, 4563
19 Masegosa, R. M., Prolongo, M. G. and Horta, A. *Macromolecules* 1986, **19**, 1478
20 Lichtenthaler, R. N., Liu, D. D. and Praustnitz, J. M. *Ber. Bunsenges. Phys. Chem.* 1974, **78**, 470
21 Galin, M. *Macromolecules* 1977 **10**, 1239
22 Summers, W. R., Tewari, Y. B. and Schreiber, H. P. *Macromolecules* 1972, **5**, 12
23 Braun, J. M. and Guillet, J. E. *Adv. Polym. Sci.* 1976, **21**, 107
24 Aspler, J. S. in 'Pyrolysis and GC in Polymer Analysis' (Chromatographic Science, Vol. 29), (Eds S. A. Liebman and E.J. Levy), Marcel Dekker, New York, 1985, p. 399
25 Delmas, G., Patterson, N. and Bhattacharyya, S. N. *J. Phys. Chem.* 1964, **68**, 1468
26 Morimoto, S. *Makromol. Chem.* 1970, **133**, 197