

Measurement of solute diffusion in polymers by inverse gas chromatography using fused-silica open tubular columns

L. Q. Xie

Analytical Research, Rohm and Haas Co., PO Box 219, Bristol, PA 19007, USA
(Received 12 January 1993; revised 7 June 1993)

Inverse gas chromatography (i.g.c.) using a fused-silica open tubular column has been developed and evaluated for measuring diffusion coefficients of small molecules in polymers; this diffusivity data can be used, for example, to model reactive extrusion processes. We have shown the applicability of this technique by measuring the diffusion and partition coefficients of various small molecules in polystyrene, poly(methyl methacrylate) (PMMA), and poly(methyl methacrylimide). The results for polystyrene and PMMA were in good agreement with existing data by gravimetric sorption/desorption, packed column and glass capillary column i.g.c. techniques. The diffusion data for the polyimide were generated for the first time.

(Keywords: inverse gas chromatography; open tubular columns; diffusion; partition)

Introduction

Diffusivity of low-molecular-weight molecules in concentrated polymers is a fundamental property frequently required for the design of many polymer synthesis and fabrication operations. For instance, diffusion (and partition) data are essential for the mathematical modelling of mass-transfer-controlled steps in an extrusion process. The rate in a mass-transfer step is strongly dependent upon diffusion of the penetrant molecules in the polymer. However, the diffusivity data are very limited, and obtaining the data over the desired temperature and concentration ranges is a formidable task.

The most common method for measuring these properties is gravimetric sorption/desorption, where a polymer sample is exposed to a constant concentration of a solute, and the diffusion coefficient is calculated by measuring the weight gain of the sample *versus* time. In addition to the relatively long time required for data collection, this method also suffers from the difficulty of measuring a constant sample geometry and the inability to analyse solutes at low concentrations.

Inverse gas chromatography (i.g.c.) has been developed recently to circumvent most of the problems associated with gravimetric methods. The non-volatile material to be investigated is used as the stationary phase in a g.c. column. This stationary phase is then characterized by monitoring the passage of volatile probe molecules, with known properties, as they are carried through the column. A number of researchers¹⁻⁶ have used packed-column i.g.c. in attempts to obtain diffusion coefficients extracted from the elution curves using the van Deemter equation. The major limitation of a packed column is the irregular distribution of the polymer, which prohibits the application of realistic models for stationary-phase transport processes. In the late 1980s, Pawlisch *et al.*^{7,8} presented a significant improvement in i.g.c. methodology for diffusion measurement; thermodynamic properties and diffusion coefficients for polystyrene and poly(methyl methacrylate) (PMMA) were obtained with the use of glass open tubular (capillary) columns.

In this study, we extend the i.g.c. method by using fused-silica open tubular (capillary) columns. The validity of the technique is shown by measuring the partition and diffusion coefficients of various solutes in polystyrene, PMMA and a polyimide. The effects of various experimental variables on i.g.c. data are also discussed.

In i.g.c., information about the interactions between a probe and a stationary phase is gathered in terms of concentration (c) and stored as a function of time (t) in the chromatogram. Integration of the raw data is performed for the first normalized moment μ_1 and the second central moment μ_2 according to the following equations:

$$\mu_1 = \frac{\int_0^\tau tc(t) dt}{\int_0^\tau c(t) dt}$$
$$\mu_2 = \frac{\int_0^\tau (t - \mu_1)^2 c(t) dt}{\int_0^\tau c(t) dt}$$

where τ is the total analysis time. The dimensionless moments are

$$\mu_1^* = \frac{\mu_1}{t_M}$$

$$\mu_2^* = \frac{\mu_2}{t_M^2}$$

where t_M is the peak retention time of an unretained solute, i.e. the (gas) hold-up time.

The first moment can be used to calculate the partition coefficient (K):

$$K = \frac{r_c(\mu_1^* - 1)}{2d_t}$$

where r_c is the radius of the gas-polymer interface, which is approximately the internal radius of the column (μm), and d_f is the polymer film thickness (μm).

This fundamental thermodynamic property (K) can then be used to determine other thermodynamic properties including the solvent activity coefficient, the Flory-Huggins interaction parameter and the solubility.

The diffusion coefficient (D) is calculated based on the dimensionless moments:

$$D = \frac{4d_f^2(1 + Q_i^2)(\mu_1^* - 1)}{3m(1 + Q_i)^2}$$

where m is the slope of the second dimensionless moment μ_2^* versus the reciprocal of the hold-up time t_M , and Q_i is the ratio of the thinnest to the thickest film dimensions observed at a particular annular cross-section of the column. References 7 to 9 provide a more detailed description of the theory and a derivation of the equations.

Experimental

A Hewlett-Packard 5790A gas chromatograph (Hewlett-Packard, Avondale, PA, USA) was used with a 225°C flame ionization detector. Both split and splitless injection modes were applied. The major modification to a conventional capillary column g.c. is the flow-control system. A flow controller (Tylan FC1000, Tylan General, Torrance, CA, USA) was selected instead of the pressure controller to provide the desired carrier gas-flow rate. A Fluke digital thermometer, with a multiple position selection switch, and four thermocouples were used for column temperature measurement. The original detector jet was replaced by a jet with a larger internal diameter so that it could fit the dimension of the columns used in this study.

The materials used were commercial grade polystyrene,

PMMA (PRD41), and poly(methyl methacrylimide) (PMMI; HT510) manufactured by Rohm and Haas Company (Bristol, PA, USA). These materials were sent to Restek Corporation (Bellefonte, PA, USA) for column preparation. All the columns were made by the static coating method using fused silica, which was used for the first time in i.g.c. studies. Fused silica is better than glass because of its stronger mechanical properties and higher intrinsic inertness. The uniformity of the columns was evaluated using a microscope, and the column dimensions, coating conditions and other characteristics of the polymeric materials are listed in Table 1. The molecular weight values given are weight-average molecular weights from gel permeation chromatography measurements. The PMMI column had a film thickness of 4 μm because of the difficulty of coating the material as a thicker (and still uniform) film inside the column.

Spectral-grade toluene, ethylbenzene, methanol, methyl methacrylate (MMA), and mono-, di- and trimethylamine were obtained from Aldrich Chemical Company (Milwaukee, WI, USA). Due to the high volatility and toxicity, amine samples were shipped as liquefied compressed gas. They were prepared in a hood by attaching a valve assembly with a vent tube to a sample bomb. The bomb was opened and approximately 1 ml of amine was allowed to bleed into a headspace g.c. sample vial (Perkin-Elmer, Norwalk, CT, USA), which then was sealed.

Results and discussion

Polystyrene. Selecting toluene and ethylbenzene as the probe molecules, we obtained partition and diffusivity data as well as the standard deviations at two temperatures (Tables 2 and 3). As expected, the first dimensionless moments (mean residence time) are independent of carrier gas velocity at both temperatures. As indicated

Table 1 Columns used for inverse gas chromatography measurements

Polymer	\bar{M}_w	Polymer density (g cm^{-3})	Polymer T_g ($^{\circ}\text{C}$)	Coating solvent	Coating temp. ($^{\circ}\text{C}$)	Coated film thickness (μm)	Column i.d. (μm)	Column length (m)
Polystyrene	1.76×10^5	1.05	93	Tetrahydrofuran	25	6.0	530	18.1
PMMA (PRD41)	1.98×10^5	1.29	118	Chloroform	25	6.0	530	17.0
PMMI (HT510)	9.73×10^4	1.43	133	Methylene chloride	40	4.0	530	18.3

Table 2 I.g.c. results from polystyrene-toluene study

Temperature ($^{\circ}\text{C}$)	Partition coefficient (standard deviation)		Dimensionless first moment (standard deviation)	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) (standard deviation)	
	Literature	Exp. ^a		Literature	Exp. ^a
120.7	at 120.2°C		3.00 (0.02)	at 120.2°C	
	64.5 (2.8) ^b	44.0 (0.4)		1.67×10^{-9} (0.06×10^{-9}) ^b	2.51×10^{-9} (0.05×10^{-9})
	66.1 (3.4) ^c			1.42×10^{-9} (0.10×10^{-9}) ^c	
140.6	at 140.6°C		2.70 (0.05)	at 140.6°C	
	38.5 (0.9) ^b	37.6 (1.0)		1.71×10^{-8} (0.06×10^{-8}) ^b	0.28×10^{-8} (0.06×10^{-8})
	38.7 (0.9) ^c			1.66×10^{-8} (0.06×10^{-8}) ^c	
				1.1×10^{-8} ^d	

^a Moment fitting was used for parameter estimation in this study. Material: $M_n = 101\,000$, $M_w = 176\,000$, $T_g = 93^{\circ}\text{C}$

^b Ref. 8. Fourier domain fitting was used for parameter estimation. Material: $M_n = 120\,000$, $M_w = 266\,000$, T_g not reported (usually 95–105°C)

^c Ref. 7. Moment fitting was used for parameter estimation

^d Ref. 14. Packed column i.g.c.

Table 3 I.g.c. results from polystyrene–ethylbenzene study

Temperature (°C)	Partition coefficient (standard deviation)		Dimensionless first moment (standard deviation)	Diffusion coefficient (cm ² s ⁻¹) (standard deviation)	
	Literature	Exp. ^a		Literature	Exp. ^a
120.7	at 120.2°C		3.50 (0.01)		
	109.9 (2.0) ^b	55.1 (0.3)		8.63 × 10 ⁻¹⁰ (0.30 × 10 ⁻¹⁰) ^b	18.0 × 10 ⁻¹⁰ (0.39 × 10 ⁻¹⁰)
	113.4 (2.3) ^c			7.30 × 10 ⁻¹⁰ (0.26 × 10 ⁻¹⁰) ^c	
140.6	at 140.6°C		3.67 (0.02)		
	64.0 (1.5) ^b	59.0 (0.3)		1.075 × 10 ⁻⁸ (3.8 × 10 ⁻¹⁰) ^b	0.702 × 10 ⁻⁸ (1.5 × 10 ⁻⁹)
	64.1 (1.5) ^c			1.048 × 10 ⁻⁸ (3.8 × 10 ⁻¹⁰) ^c	

Footnotes as for Table 2

previously^{10,11}, median or maximum retention time values are easier to obtain than the mean retention time, but may lead to serious errors in thermodynamic property determination. They are inappropriate for calculating K when strong mass-transfer resistances are present and therefore were not used in this study. Moreover, in contrast to the previous capillary column i.g.c. work⁷, we obtained a strong correlation between dimensionless moments (μ_1^* and μ_2^*) and carrier velocity for all the data sets. Rather small variations were observed for the first dimensional moments. This is largely attributed to the good flow control in the system and an appropriate baseline correction used in the data-truncation program. The second dimensionless moments (variance about the mean retention time) show linear relations with the inverse hold-up time. Then the slopes were used to calculate the diffusion coefficients at preset temperature.

The results were compared with those from literature using various methods, such as gravimetric vapour sorption^{12,13}, packed¹⁴ and capillary⁷⁻⁹ column i.g.c. (Tables 2 and 3). Vapour sorption data are not listed because exact values are not available. However, the vapour sorption curves were extrapolated to obtain diffusivity at an infinitely dilute probe concentration, and the value was consistent with other studies. Despite the fact that several magnitudes of variation can easily be made for such low diffusivity measurement, our data show good agreement with the literature values in general. Diffusion coefficients (D) at both temperatures are within one order of magnitude of the previous work. Lower partition coefficients (K) at 120°C and some differences in D were observed, which are believed to be due to differences in the materials tested (lower molecular weight and probably lower glass transition temperature, T_g , material was used in this work; refer to Table 2 for details). Frequently, diffusivity has a strong temperature dependence in polymers near but above their T_g ¹⁵. As temperature rises further, however, space between the molecules (free volume) is no longer increased so rapidly. This explains why the diffusivity does not increase obviously from 120 to 140°C, because both temperatures are well above the T_g of the material used in this work (93°C). T_g was not reported in the literature^{7,14}, thus it was hard to evaluate the impacts of T_g on diffusivity. Nevertheless, despite the differences shown in Tables 2 and 3, the trends were very similar for the two probes.

PMMA and PMMI. Tables 4 and 5 summarize the i.g.c. results for methanol and trimethylamine in PMMA,

and Tables 6–8 for methanol, trimethylamine and MMA in PMMI. For comparison, Table 8 also includes the diffusivities of MMA in PMMA over a broad temperature range.

The PMMA–methanol data were compared directly with Pawlisch *et al.*'s i.g.c. work⁸ (exactly the same material, PRD41, was used) and indirectly with Duda *et al.*'s vapour sorption study^{12,13}. Despite the slower diffusion (and more skewed elution curves) in PMMA than in polystyrene, both the partition and diffusion coefficients are highly consistent with the literature. In fact, this polymer–probe system was found to be very reliable within relatively broad temperature and flow rate ranges, and can thus be used as a monitor for open tubular column i.g.c.

Similar measurements were then extended to PMMA with trimethylamine as a probe, which to our knowledge has never been studied before. Trimethylamine was injected into the g.c. column by a 0.5 μ l syringe precooled in dry ice. From the results listed in Table 5, we can see that trimethylamine has a smaller diffusion coefficient than methanol in PMMA. This was expected, since a larger molecule should exhibit a lower diffusivity.

A Williams–Landel–Ferry relationship, $\log D$ versus $1/(A_{22} + T - T_g)$, was used to describe the temperature dependence of D . It is a more adequate approach than the Arrhenius equation, as discussed previously^{8,13}.

For PMMI, all the probes (methanol, trimethylamine and MMA) showed linearity between the second moments and the reverse hold-up time, and the slopes were used to obtain D (Tables 6–8). Similarly, the measurements for the PMMI–methanol system were made at temperatures both above and below T_g ; the data for the system were reliable within broad temperature and flow rate ranges and were very reproducible over time. The D data generated in this work combined with the modified free-volume theory¹³ can be used for diffusivity prediction at any temperature above T_g . For comparison, the diffusion coefficients of methanol and trimethylamine in PMMA and PMMI at 250°C are predicted and listed in Table 9. It can be seen that at the given temperature, the D values of the same probes in the two polymers are within one order of magnitude. By comparing the thermodynamic properties obtained earlier, we also found the partition coefficients of methanol and trimethylamine in these two materials to be very close, with that of MMA only slightly different (lower in PMMI).

It is well known that diffusivity depends on temperature, the size and the concentration of the probe selected, and

Table 4 I.g.c. results from PMMA–methanol study

Temperature (°C)	Partition coefficient (standard deviation)		Dimensionless first moment (standard deviation)	Diffusion coefficient (cm ² s ⁻¹) (standard deviation)	
	Literature	Exp. ^a		Literature	Exp. ^a
90.1	at 89.8°C 28.56 ^b	27.77 (0.07)	2.131 (0.003)	1.78 × 10 ⁻⁹ ^b	1.86 × 10 ⁻⁹ (0.39 × 10 ⁻⁹)
100.6	at 100.3°C 19.81 ^b	18.17 (0.06)	1.820 (0.003)	3.14 × 10 ⁻⁹ ^b	3.42 × 10 ⁻⁹ (0.68 × 10 ⁻⁹)
110.7	at 109.7°C 14.80 ^b	13.15(0.06)	1.595 (0.003)	6.02 × 10 ⁻⁹ ^b	9.39 × 10 ⁻⁹ (2.1 × 10 ⁻⁹)
		12.71(0.15)	1.580 (0.010)	6.02 × 10 ⁻⁹ ^b	6.80 × 10 ⁻⁹ (1.5 × 10 ⁻⁹) ^d
130.7	at 130.4°C 8.68 ^b	8.79 (0.06)	1.398 (0.003)	2.10 × 10 ⁻⁸ ^b 8.29 × 10 ⁻⁸ ^c	4.26 × 10 ⁻⁸ (0.94 × 10 ⁻⁸)
150.8	at 150.7°C 6.72 ^b	6.50 (0.05)	1.294 (0.002)	7.23 × 10 ⁻⁸ ^b	7.73 × 10 ⁻⁸ (1.60 × 10 ⁻⁸)
160.9	at 160.8°C 5.84 ^b	5.34 (0.03)	1.242 (0.001)	1.19 × 10 ⁻⁷ ^b	1.74 × 10 ⁻⁷ (0.38 × 10 ⁻⁷)

^a Moment fitting was used for parameter estimation in this study

^b Ref. 8. Only Fourier domain fitting was used in the literature and no standard deviation data were available. Same PMMA material (PRD41) was used here and in ref. 8

^c Ref. 17. Gravimetric sorption/desorption method was used in the literature and the data were measured at a finite concentration of 0.191 wt%

^d Data obtained 1 month later for reconfirmation

Table 5 I.g.c. results from PMMA–trimethylamine study

Temperature (°C)	Partition coefficient (standard deviation)	Dimensionless first moment (standard deviation)	Diffusion coefficient (cm ² s ⁻¹) (standard deviation)
120.7	0.0856 (0.0740)	1.025 (0.008)	5.19 × 10 ⁻⁹ (1.14 × 10 ⁻⁹)
135.7	0.1296 (0.0240)	1.021 (0.007)	1.61 × 10 ⁻⁹ (0.35 × 10 ⁻⁹)
150.8	0.2236 (0.0521)	1.017 (0.004)	3.76 × 10 ⁻⁸ (0.83 × 10 ⁻⁸)

Table 6 I.g.c. results from PMMI–methanol study

Temperature (°C)	Partition coefficient (standard deviation)	Dimensionless first moment (standard deviation)	Diffusion coefficient (cm ² s ⁻¹) (standard deviation)
105.5	19.09 (0.69)	1.561 (0.035)	1.28 × 10 ⁻⁹ (0.22 × 10 ⁻⁹)
115.7	13.60 (0.40)	1.410 (0.012)	2.51 × 10 ⁻⁹ (0.43 × 10 ⁻⁹)
125.5	10.65 (0.16)	1.321 (0.005)	4.36 × 10 ⁻⁹ (0.74 × 10 ⁻⁹)
140.6	8.44 (0.05)	1.255 (0.001)	1.00 × 10 ⁻⁸ (0.17 × 10 ⁻⁸)
160.8	6.15 (0.01)	1.186 (0.001)	3.09 × 10 ⁻⁸ (0.56 × 10 ⁻⁸)
180.6	4.60 (0.05)	1.139 (0.001)	7.94 × 10 ⁻⁸ (1.40 × 10 ⁻⁸)

Table 7 I.g.c. results from PMMI–trimethylamine study

Temperature (°C)	Partition coefficient (standard deviation)	Dimensionless first moment (standard deviation)	Diffusion coefficient (cm ² s ⁻¹) (standard deviation)
140.6	0.3078 (0.0956)	1.009 (0.003)	3.51 × 10 ⁻⁹ (0.77 × 10 ⁻⁹)
155.6	0.3375 (0.0351)	1.010 (0.001)	6.38 × 10 ⁻⁹ (1.40 × 10 ⁻⁹)
170.6	0.9619 (0.0374)	1.029 (0.001)	1.01 × 10 ⁻⁸ (0.22 × 10 ⁻⁸)

certainly the type of polymer material tested. Our polystyrene data, when compared to the literature, show that a difference in diffusion can be seen when using the same types of material but with different molecular weights. The close data for the PMMA and PMMI

further show that besides molecular weight, density and other properties can also affect diffusivity. These effects on diffusion are normally not as direct and significant as the well-known factors; the effects could even cancel each other out under certain conditions. However,

Table 8 I.g.c. results from PMMI–MMA and PMMA–MMA studies

Temperature (°C)	Partition coefficient (standard deviation)	Dimensionless first moment (standard deviation)	Diffusion coefficient (cm ² s ⁻¹) (standard deviation)
PMMI			
135.6	9.40 (1.11)	1.284 (0.034)	2.04 × 10 ⁻⁹ (0.41 × 10 ⁻⁹)
150.6	2.93 (0.28)	1.091 (0.009)	3.70 × 10 ⁻⁹ (0.74 × 10 ⁻⁹)
165.6	1.18 (0.12)	1.036 (0.004)	4.88 × 10 ⁻⁹ (0.98 × 10 ⁻⁹)
PMMA			
60.1	–	–	2.88 × 10 ⁻¹³
80.2	–	–	2.75 × 10 ⁻¹²
135.6	–	–	2.29 × 10 ⁻¹⁰
150.6	–	–	1.25 × 10 ⁻⁹
165.6	–	–	3.96 × 10 ⁻⁹

Table 9 Prediction and comparison of diffusion coefficient in PMMA and PMMI at 250°C

Probe	Polymer	Diffusion coefficient (cm ² s ⁻¹)
Methanol	PRD41	9.38 × 10 ⁻⁷
	HT510	1.17 × 10 ⁻⁶
Trimethylamine	PRD41	4.34 × 10 ⁻⁷
	HT510	1.20 × 10 ⁻⁷

they do contribute individually to the difference in the elution curves and thus in i.g.c. results. This, in fact, reflects the usefulness and potential of i.g.c. in polymer characterization.

According to the assumptions proposed by Macris¹⁶ to analyse an elution curve, a probe should be selected so that there is no surface adsorption or chemical reaction between the probe and the polymer. We actually tried to measure the diffusion of monomethylamine in PMMA, but the data turned out to be meaningless. We believe that this is due to a chemical reaction between the probe and the polymer that occurred during the i.g.c. experiment. Although the experiment was performed at probe concentrations approaching infinite dilution and no peak of the reaction product was detected, the elution peak was severely skewed and thus led to poor precision of *D* results. Although not able to measure *D* directly for some polymer–solvent systems, i.g.c. can still provide a ‘window’ for diffusivity by combining the experimental data of other systems and the free-volume theory modified for diffusivity prediction^{12,13}. According to the theory, diffusivity of monomethylamine should be between that of methanol and trimethylamine under the same conditions because of their molecular size order. From *Table 9*, the diffusion coefficient of monomethylamine in PMMA is predicted to be between 4.34 × 10⁻⁷ and 9.38 × 10⁻⁷ cm² s⁻¹ at 250°C.

To ensure accurate measurements in i.g.c., one must adequately select or control the following experimental conditions: column film thickness and uniformity, injection mode and amount, temperature, flow rate and data handling. Flow-rate control and data handling are discussed in more detail.

Flow control is more appropriate than pressure control in an i.g.c. study, especially for systems with low diffusivities. Furthermore, all measurements should be

made at low flow rates, otherwise increased skewing and more tailing of the elution curves will result. Most capillary column g.c. equipment comes with pressure control, which cannot control a constant flow at low flow rates. To overcome this problem, we replaced the original pressure-control system with a gas-flow controller which is capable of regulating helium flow to ±1% for flows at 2 ml min⁻¹.

A large part of i.g.c. studies consists of data manipulation. Initially, data were collected on a Perkin–Elmer–Nelson system and then dumped to a personal computer via PCTalk. Later, the data collection system was replaced by a VAX-based Perkin–Elmer–Nelson ACCESS*CHROM system so that data could be accessed directly. The data acquisition frequencies are normally 5–20 data points per second, depending on the peak width and symmetry. The reliability of the parameter estimation decreases as tailing in the elution curve increases. This is caused by the loss in precision of the data in the tail of the curve due to the low signal-to-noise ratios. The moment parameter estimation works well when elution curves are symmetric (or nearly so), with well-defined end points. However, moment analysis may lead to significant errors for serious skewing or tailing curves; this is because of the difficulty in the nature of weighing functions used to calculate moments. The solutions for the problem include selecting appropriate column geometry and low flow rates, and double-checking data files before and after running the data-truncation program. Other parameter estimation methods, such as Fourier domain fitting⁹, are recommended when necessary.

Conclusions

Studying solute diffusion in polymers by open tubular column i.g.c. is a relatively new research area. The methodology was developed and applied to a polyimide material for the first time; i.g.c. has again proved to be a useful tool for measuring the characteristic properties of polymers. Simplicity, ruggedness, low cost, speed of analysis and wide availability of equipment (g.c.) are its major advantages. Properties with a variety of probes can be measured over a broad temperature range. In comparison with other methods (neutron scattering, solvent swelling, gravimetric sorption, etc.), i.g.c. is ideal for studying dilute solutes in concentrated polymers, copolymers, polymer blends, glass and carbon fibres, coal,

solid food, and so on. Experimental data can be combined with a modified free-volume theory to generate new data, which allow the prediction of diffusivity at conditions that are unreachable (e.g. very high temperature) or even for unknown polymer-probe systems. It should also be noted that this method is not applicable to high concentrations of probes in polymers. Another limitation is the difficulty of coating high quality columns with some polymer materials.

Acknowledgement

The author thanks Professor R. L. Laurence for helpful discussions.

References

- 1 Taint, P. J. T. and Abushihada, A. M. *J. Chromatogr. Sci.* 1979, **17**, 219
- 2 Braun, J. M., Poos, S. and Guillet, J. E. *Polym. Lett.* 1976, **14**, 257
- 3 Kong, J. M. and Hawkes, S. J. *Macromolecules* 1975, **8**, 148
- 4 Miller, W. and Hawkes, S. J. *J. Chromatogr. Sci.* 1977, **15**, 148
- 5 Galin, M. and Rupprecht, M. C. *Polymer (Am. Chem. Soc., Div. Polym. Chem.)* 1978, **19**, 506
- 6 Senich, G. A. *Polym. Prepr.* 1981, **22** (2), 343
- 7 Pawlisch, C. A., Macris, A. and Laurence, R. L. *Macromolecules* 1987, **20**, 1564
- 8 Pawlisch, C. A., Bric, J. R. and Laurence, R. L. *Macromolecules* 1988, **21**, 1685
- 9 Pawlisch, C. A. PhD Dissertation, University of Massachusetts at Amherst, 1985
- 10 Galin, M. and Rupprecht, M. C. *Polymer (Am. Chem. Soc., Div. Polym. Chem.)* 1978, **19**, 506
- 11 Newman, R. D. and Prausnitz, J. M. *J. Phys. Chem.* 1972, **76**, 1492
- 12 Duda, J. L., Ni, C. Y. and Vrentas, J. S. *J. Appl. Polym. Sci.* 1978, **22**, 289
- 13 Duda, J. L., Vrentas, J. S., Ju, S. T. and Liu, H. T. *AIChE J.* 1982, **28**, 279
- 14 Romdhane, J. H. Presentation at Center for the Study of Polymer Solvent Diffusion and Phase Equilibria Behavior, Pennsylvania State University, State College, PA, September 1990
- 15 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 403
- 16 Macris, A. MS Thesis, University of Massachusetts at Amherst, 1979
- 17 Ju, S. T., Liu, H. T., Duda, J. L. and Vrentas, J. S. *J. Appl. Polym. Sci.* 1986, **26**, 3735