# A light scattering study of a main chain aromatic polyester in mixed solvents

## W. A. MacDonald
*ICI plc, Wilton Materials Research Centre, PO Box 90, Wilton, Middlesbrough, Cleveland, UK*

## and A. D. W. McLenaghan and R. W. Richards*
*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK*

The dilute solution properties of a main chain aromatic polyester in a co-solvent mixture (trifluoroacetic acid/dichloromethane) have been investigated. Nine separate fractions in six co-solvent mixtures have been studied by differential refractometry and low angle laser light scattering. It has been shown that trifluoroacetic acid is preferentially adsorbed by the polymer. Light scattering data indicates that the polymer has a random coil configuration in solution and values for the polymer–solvent interaction parameter have been extracted. From the data we have obtained $(\langle r^2 \rangle_0 / M)^{1/2} = 7.72 \times 10^{-9}$ cm. This ratio is discussed with reference to other values for aromatic polyesters.

## INTRODUCTION

In recent years much interest has developed in the properties, structural organization and applications of main chain liquid crystal polymers[1]. This has been prompted by the prospect of obtaining polymeric materials with very high modulus but low density. Among the well known examples of these polymers are the aromatic polyamides. All of these polymers exhibit a nematic phase in concentrated solution or over a finite temperature range in the bulk state. On cooling from the nematic melt this mesogenic order is retained and considerable effort has been expended on the theoretical and experimental investigation of the molecular and super-molecular organization of liquid crystal polymers[2].

By contrast, knowledge regarding the molecular characterization of such polymers is sparse. This is largely due to the insolubility of these polymers in common solvents. Frequently, ferocious solvent conditions have to be used and these can introduce additional problems, e.g. very high temperatures, absorption of atmospheric moisture. In the dilute solution studies of poly 1,4-phenyleneterephthalamide[3,4] and poly 1,4-phenylene-2,6-benzobisthioazole[5] in sulphuric acid or methane sulphonic acid, the polymer protonated to form macroions and there was evidence of molecular aggregation. Krigbaum[6,7] has reported the dilute solution behaviour of two other liquid crystal polymers, where the solvent conditions were not so severe. In common with many liquid crystal polymers, all of the systems referred to above have phenylene groups as part of the main chain backbone and many are copolymers, being prepared from two separate monomer units. However, in the cases

referred to thus far it is evident that the two monomer units repeat alternately along the chain. Light scattering data on all of these polymers clearly indicated the rod-like nature of the molecules, even in dilute solution, and much effort was devoted to measurement of the molecular anisotropy and evaluation of the persistence length of the semi-flexible molecules.

We discuss here the molecular characterization, using light scattering, of a terpolymer. In the bulk state this terpolymer (denoted as LCP here) has a nematic phase for temperatures $> 540$ K and appears to align over large length scales when extruded in the melt phase. LCP is an aromatic polyester and consequently strong mineral acids are excluded as possible solvents. However, it has been found to be soluble in mixtures of trifluoroacetic acid (TFA) and dichloromethane (DCM) over a wide range of solvent composition. The polymer is insoluble in either of the solvent components alone. Hence there are three possible aspects to the dilute solution investigation of this polymer:

(1) evaluation of the molecular parameters, e.g. unperturbed dimensions, binary cluster integral and molecular anisotropy;

(2) assessment of compositional heterogeneity in the random terpolymer as well as molecular weight heterogeneity; and

(3) investigation of preferential adsorption of one or other solvent components to gain some insight into the co-solvency.

Additionally, unlike the polymers discussed above, LCP is not a strictly linear molecule since a proportion of linkages *meta* to each other on the phenyl rings are deliberately incorporated into the main chain backbone.

* To whom correspondence should be addressed at Department of Chemistry, Durham University, Durham DH1 3LE, UK

## THEORY

### Light scattering from semi-rigid molecules

Berry[8] has reviewed the properties of light scattered from solutions of optically anisotropic polymers. Equations have been presented by him, and others[3], pertaining to vertically polarized incident light and solutions wherein the polymer molecules have a molecular anisotropy, $\delta$. The horizontally and vertically polarized components of the excess Rayleigh ratio, for light scattered at an angle $\theta$ to the incident beam, are given by $R_{VV}(\theta)$ and $R_{HV}(\theta)$, respectively. We have

$$\lim_{\theta \to 0} K^*c/R_{VV}(\theta) = 1/[M_w(1 + 4/5 - \delta^2)$$
$$+ 2A_{2c}/[1 + (4/5)\delta^2]] \quad (1)$$

$$\lim_{\substack{\theta \to 0 \\ c \to 0}} K^*c/R_{HV}(\theta) = 3\delta^2/5 \quad (2)$$

where:

$K^* = 4\tilde{n}_0^2 v^2/\lambda_0^4 N_A$;
$\tilde{n}_0$ = refractive index of solvent;
$\lambda_0$ = wavelength of incident light *in vacuo*;
$v$ = specific refractive index increment (s.r.i.i.) of polymer in solution;
$N_A$ = Avogadro's number.

The value of $\delta$ is determined by the ratio of the persistence length to the contour length of the molecule. For true rigid molecules this ratio is infinite, while for random coil molecules the value is reduced.

### Light scattering from terpolymers

It has been well known for many years that the excess Rayleigh ratio of copolymer solutions is dependent on the composition distribution of the copolymer molecules. Detailed equations relating the excess Rayleigh ratio to parameters characterizing the compositional heterogeneity were obtained by Bushuk and Benoit[9] and there has subsequently been considerable experimental investigation of these equations[9-12]. Of particular note is the fact that light scattering from copolymer solutions produces an apparent value of molecular weight, unless special conditions are used (i.e. s.r.i.i. of copolymer components are equal). Consequently, for binary copolymers, evaluation of the true molecular weight necessitates the use of three solvents wherein the copolymer components have different s.r.i.i. The apparent molecular weight is given by

$$M_{app} = v^{-2} \sum_i v^2 M_i w_i \quad (4)$$

where $v$ = average s.r.i.i. of the copolymer and $v_i$ = s.r.i.i. of copolymer species with a molecular weight $M_i$, present in the copolymer at a weight fraction $w_i$. For terpolymers, the relevant equation for the apparent molecular weight has six unknowns[13] (one being the true molecular weight) and consequently calculation of true molecular weight requires excess Rayleigh ratios to be measured in six solvents wherein the s.r.i.i. of the individual components differ. For a terpolymer consisting of units A, B and C, the equation for $M_{app}$ is given by

$$M_{app} = M_w + 2P_A(v_A - v_C)/v + 2P_B(v_B - v_C)/v$$
$$+ Q_A[(v_A - v_C)/v]^2 + Q_B[(v_B - v_C)/v]^2$$
$$+ 2R[(v_A - v_C)/v][(v_B - v_C)/v] \quad (5)$$

where

$M_w$ = true weight average molecule weight
$\quad = \sum_i M_i w_i$

$$P_A = \sum_i M_i w_i (\delta w_{Ai}) \quad (6)$$

$$P_B = \sum_i M_i w_i (\delta w_{Bi}) \quad (7)$$

$$Q_A = \sum_i M_i w_i (\delta w_{Ai})^2 \quad (8)$$

$$Q_B = \sum_i M_i w_i (\delta w_{Bi})^2 \quad (9)$$

$$R = \sum_i M_i w_i (\delta w_{Ai})(\delta w_{Bi}) \quad (10)$$

where the $\delta_{wji}$ terms are the deviations in compositions of component $j$ in species $i$ molecules.

## EXPERIMENTAL

### Polymer

The main chain aromatic polyester (LCP) was supplied by ICI plc, Advanced Materials. It is a terpolymer with residues of *p*-hydroxybenzoic acid (HBA), hydroquinone (HQ) and isophthalic acid (IPA) in a random sequence in the molecule. The stoichiometric composition of the polymer is as shown below:
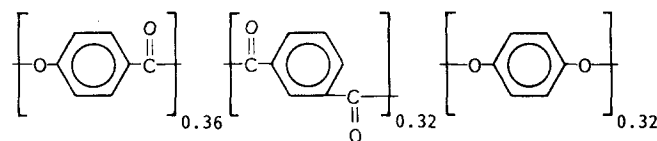


As received, this polymer is in the form of chips, which were subsequently dissolved in a mixture of trifluoroacetic acid (TFA) and dichloromethane (DCM) with a TFA volume fraction of 0.80. Solutions with a polymer concentration of $\approx 2\%$ (w/v) were centrifuged at 8000 rev min$^{-1}$ for 2 h, the temperature being maintained at 288 K. After centrifugation, the clear supernatant liquid was removed from the solid debris at the bottom of the tube by careful pipetting. The supernatant liquid was then re-centrifuged and filtered through a 0.2 $\mu$m pore diameter Teflon membrane and finally poured into rapidly stirred 2-butanone to precipitate the polymer. After filtering, the polymer was dried for 48 h under vacuum at a temperature of 373 K before it was stored in a desiccator. The polymer was then in the form of a white powder.

### Solvents

The solvents used in this work, TFA, DCM and 2-butanone were dried over anhydrous magnesium sulphate and distilled at atmospheric pressure. The first 10% distilling over was rejected and distillation ceased when 20% of the original volume was left in the distillation flask. For TFA the boiling point recorded was 345.5 K while that of DCM was 314.1 K.

### Fractionation

A large (2 l) three-necked round-bottomed flask was fitted with a stirrer and a narrow inlet tube directed at the vortex created by the stirrer. A solution of LCP ($\approx 2\%$ w/v) in TFA 0.8/DCM 0.2 was placed in the flask and
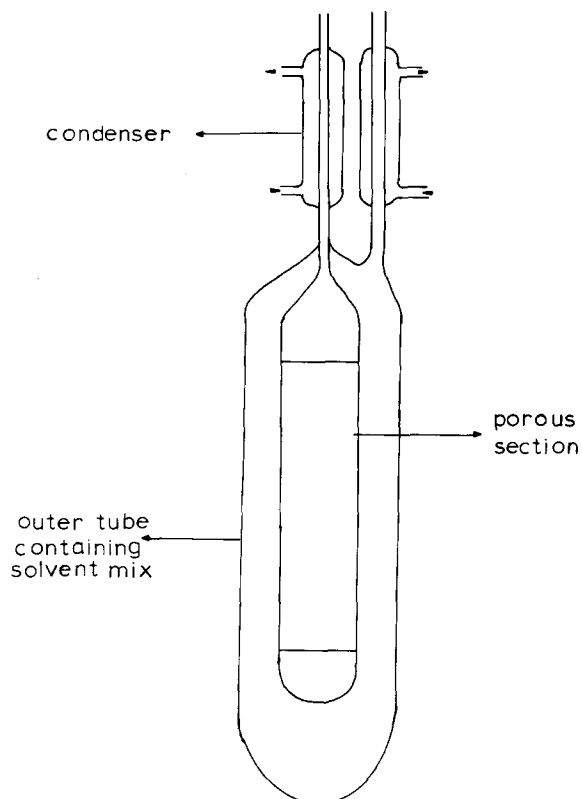
**Figure 1** Schematic diagram of all-glass dialysis cell used for determination of specific refractive index increment at constant chemical potential

stirred rapidly. Precipitant (2-butanone) was added slowly until the solution became cloudy. At this point the mixture continued to be stirred for 24 h to ensure equilibrium precipitation and re-dissolution of LCP. Stirring was then ceased and the solution plus precipitate centrifuged to separate them. The clear supernatant was then carefully withdrawn and placed in a second, identical flask. Addition of the mixed (TFA 0.8/DCM 0.2) solvent to the washed and dried fraction precipitated caused it to redissolve after which it was reclaimed by pouring it into a large excess of well stirred 2-butanone. The LCP fraction was filtered off and dried as for the parent polymer described above. This whole process was repeated on the supernatant fluid and in this manner we obtained nine LCP fractions, each with a mass of $\approx 2$ g.

*Refractive index*

Refractive indices ($\tilde{n}_0$) of pure TFA and DCM and mixtures of varying volume fraction of TFA were measured at 298 K using a Pulfrich refractometer with a mercury lamp as light source. Values were obtained at wavelengths of 435.8, 546.1, 579.1 and 643.8 nm, respectively, for each solution. The value of $\tilde{n}_0$ at 632.8 nm was interpolated from a Cauchy dispersion plot of $\tilde{n}_0$ as a function of $\lambda^{-2}$. These plots were always linear.

*Specific refractive index increments*

Values of s.r.i.i. were obtained using solutions of an LCP fraction with molecular weight $\approx 101\,500$ and a Brice–Phoenix differential refractometer modified to provide light with a wavelength of 632.8 nm. Values were obtained for constant solvent composition ($v_\phi$) and for constant chemical potential of the solvent mixture ($v_\mu$).

Readings were taken for five different concentrations of LCP between 0.2 and 1.5% (w/v) and values of s.r.i.i. obtained from plots of $\Delta\tilde{n}$ as a function of $c$ and $\Delta\tilde{n}/c$ as a function of $c$, where $\Delta\tilde{n}$ is the refractive index difference between solution and solvent and $c$ the concentration of LCP in g ml$^{-1}$.

To obtain values of $v_\mu$, the polymer solutions were dialysed against the solvent mixture and measurements made with reference to the dialysate. Due to the powerful nature of the solvent mixture, the simple cellulose dialysis bags often used[14] could not be utilized for the system here. Consequently, we devised[15] the dialysis cell shown in *Figure 1* where the inner cell is constructed from porous Vycor® glass tubing. The pores in this tubing are 5.0 nm in diameter and the wall thickness is 1 mm. From separate experiments, the time to reach dialysis equilibrium was determined to be 10 d and no evidence was found of polymer diffusing through the pores. Because of the necessarily long dialysis equilibration times and the volatile nature of the DCM component in the solvent mixture, water at 275 K was circulated through the small condensers which formed part of the dialysis cells. To prevent water condensing from the atmosphere into the component parts of the dialysis cell, tubes filled with calcium chloride were mounted on the two condensors. The lower part of the dialysis cell, which included the porous tube, was immersed in a thermostat at 298 K and all measurements of $v_\phi$ and $v_\mu$ were also made at 298 K.

*Density of solvent mixtures and LCP solutions*

Densities of mixtures of TFA and DCM were measured at 298.15 K using a Paar digital densitometer, Model DMA 602. Densities of LCP solutions in solvent mixtures were also obtained by the same method and at the same temperature, the range of LCP weight fractions used being $0.005 \leqslant w_{\text{LCP}} \leqslant 0.03$.

*Static light scattering*

Measurements of the excess scattered light intensity from solutions of the LCP polymer in various mixtures of TFA and DCM were made using a Chromatix KMX-6 low angle laser light scattering photometer. The principles of this instrument have been described elsewhere[16]. Before use, the attenuators and pentaprism were cleaned with distilled 2-butanone and the quartz window blocks were soaked in permanganic acid. After drying and final cleaning of the windows of the quartz blocks with 2-butanone, the cell and in-line filter were assembled. Solutions were first pre-filtered through a 0.2 μm PTFE membrane before being filtered directly into the scattering volume through the in-line membrane filter with a pore size of 0.2 μm. The nominal scattering angle used was 6–7° but, because the actual scattering angle depends on the refractive index of the solution, the actual scattering angle was in the neighbourhood of 4.6°. The precision and accuracy of the instrument were ascertained by measurement of the Rayleigh ratio of specially purified toluene. The value obtained was always within 2% of the value quoted in the literature[16]. Absolute values of the Rayleigh ratio were calculated from the instrument factors and the measured photocurrent. For molecular weight and second virial coefficient determinations, the concentrations of LCP fraction used were between 0.05 and 0.6% (w/v) in the solvent mixtures utilized.
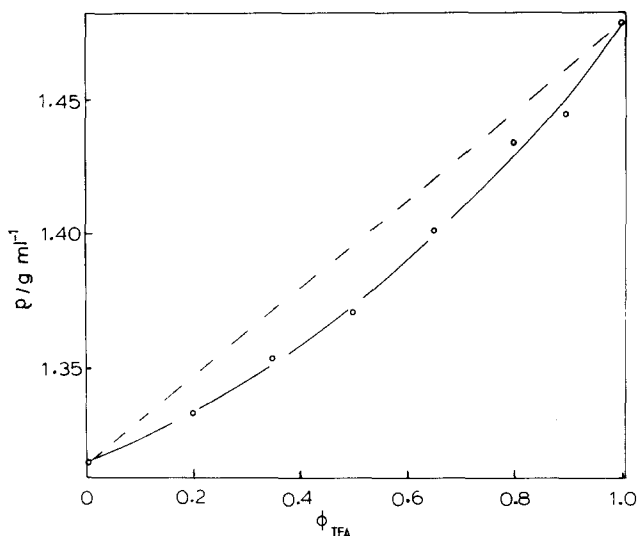
**Figure 2** Density of TFA/DCM mixtures at 298.1 K as a function of TFA volume fraction
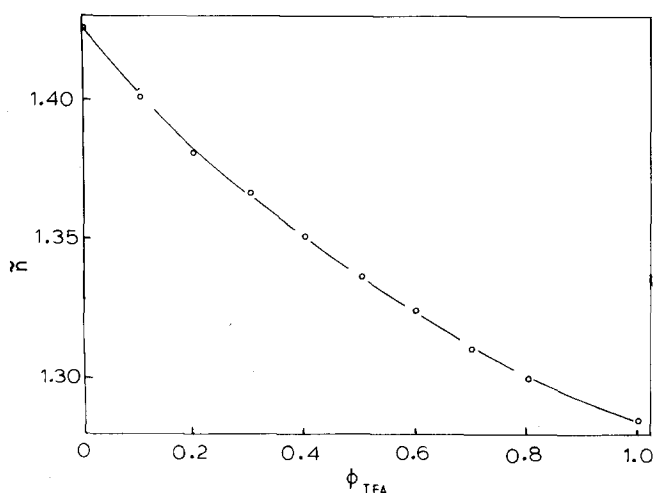


**Figure 3** Refractive index at 298.15 K for TFA/DCM mixtures for light of wavelength 632.8 nm

## RESULTS

### Refractive index of solvent mixtures and polymer components

*Figure 2* shows the variation in density of the solvent mixture over the mixed solvent composition range investigated. Marked negative deviations from strict volume additivity are evident. These are attributable to partial molar volume effects in the solvent mixture. This non-linear dependence of density on solvent composition is reflected in the dependence of refractive index on composition (*Figure 3*). The refractive indices of the individual monomer units were calculated via the Gladstone–Dale equation using group molar refractivities[17],*. Although these refractive index values are only approximate, they were sufficient to indicate the likelihood of success in any attempt to determine the heterogeneity parameters ($P$, $Q$ and $R$) of the terpolymer. For a light wavelength of 589 nm, we obtained values of

---

* Although values for the group molar refractivities at $\lambda = 633$ nm can be interpolated from data of Eisenlohr[18], they do not take account of the differences which become apparent when groups are attached to phenylene rings. Consequently values for $\lambda = 589$ nm have been used

1.631, 1.659 and 1.626 for the refractive indices of the HBA, IPA and HQ residues, respectively, from this calculation.

### Specific refractive index increments

The variation of $v_\phi$ with $n_0$ for LCP in TFA/DCM solutions with varying composition is linear; the least squares line through the data yields the relation

$$v_\phi = 1.6846 - 1.0689\tilde{n}_0 \qquad (11)$$

with a correlation coefficient of $-0.99$. Many equations have been proposed relating $v$ to the refractive index of the solvent, usually in terms of the specific refraction, $R$, which is a product of the partial specific volume and a function of the refractive index of the components of the solution. The simplest of these refractive index expressions is the Gladstone–Dale equation:

$$v = v_2(\tilde{n}_p - \tilde{n}_0) \qquad (12)$$

where $v_2$ is the partial specific volume of the polymer which has a refractive index $\tilde{n}_p$. Applying equation (12) to the $v_\phi$ data yields a value of 1.5760 for the refractive index of the polymer at 25°C and a wavelength of 632.8 nm. The partial specific volume obtained is 1.069 ml g$^{-1}$, which is an average value over all the solvent mixtures used, and may well vary depending on the solvent composition (see below).

For the same TFA/DCM mixtures, the s.r.i.i. at constant chemical potential ($v_\mu$) were also measured. *Figure 4* shows that $v_\mu$ increases rapidly for $\phi_{TFA} > 0.4$. With the values of $v_\phi$ and $v_\mu$, the preferential adsorption parameter ($\alpha_{TFA}$) for the adsorption of the TFA into the vicinity of the LCP molecule can be calculated from the relation[19]

$$\alpha_{TFA} = (v_\mu - v_\phi)/(d\tilde{n}_0/d\phi) \qquad (13)$$

Values of ($d\tilde{n}_0/d\phi$) were obtained from the data of *Figure 3* by taking the slopes of lines tangential to the smooth curve through the data at the volume fraction of TFA used. *Figure 5* shows the variation of $\alpha_{TFA}$ with volume fraction of TFA in the mixture. For the solvent compositions investigated TFA is always preferentially adsorbed although, over the range $0.2 \leqslant \phi_{TFA} \leqslant 0.8$ the



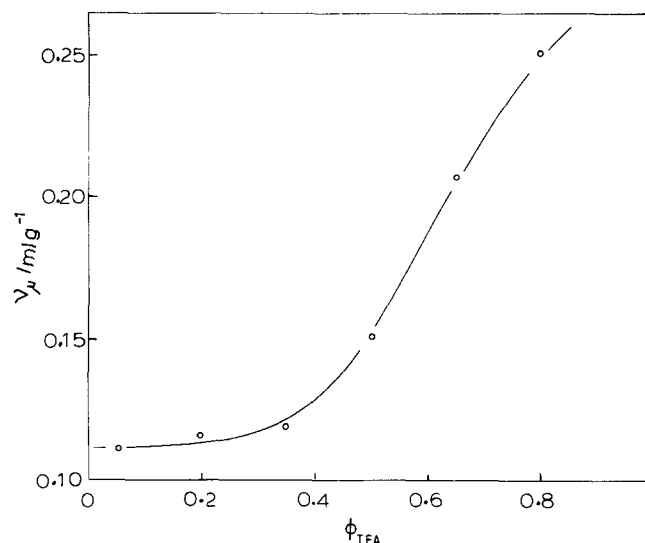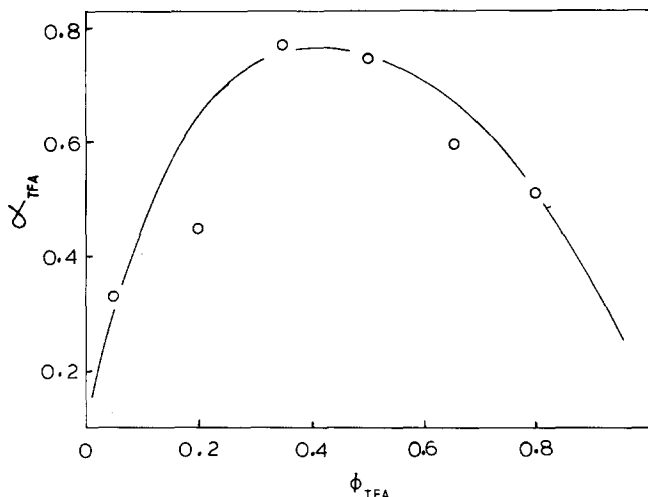**Figure 4** Specific refractive index increments of LCP at constant chemical potential and 298.15 K as a function of volume fraction of TFA

**Figure 5** Preferential adsorption coefficient for the adsorption of TFA onto LCP as a function of TFA volume fraction



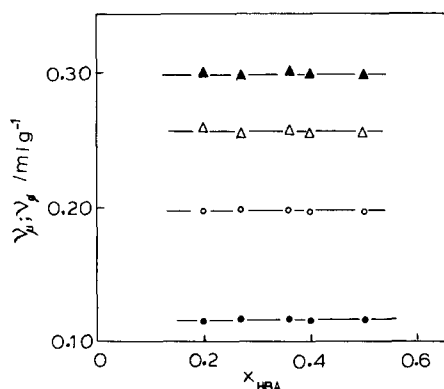**Figure 6** Values of $v_\mu$ and $v_\phi$ (at 298.15 K) for LCP terpolymers with differing HBA content. O, △, Constant chemical potential; ●, ▲, constant solvent composition. O, ●, $\phi_{TFA} = 0.2$; △, ▲, $\phi_{TFA} = 0.8$

value of $\alpha_{TFA}$ does not vary greatly. However, it should be pointed out that the magnitudes of the $\alpha_{TFA}$ values obtained are considerably larger than those obtained for more conventional ternary systems, e.g. polymer + solvent + non solvent[20,21].

The refractive indices calculated for the components of the terpolymer indicated that they were not sufficiently different for the evaluation of the heterogeneity parameters. To confirm this, values of $v_\mu$ were measured for five LCP polymers with different mole fractions of HBA. *Figure 6* shows the dependence of $v_\mu$ and $v_\phi$ on HBA content for these polymers in two solvent mixes. In both cases, there is no discernible dependence of $v_\mu$ on polymer composition. Hence we conclude that, within the accuracy of our differential refractometer, the three components of the polymer have equal specific refractive index increments. Consequently, there is no prospect of using equations (5)–(10) to evaluate heterogeneity parameters and, because the $v_\mu$ were essentially identical for all components, the molecular weight obtained by light scattering is the true molecular weight.

*Partial specific volume of LCP*

The partial specific volume of LCP in the TFA/DCM mixtures used for light scattering were obtained from the densities of LCP solutions. These data were plotted according to equation (14)[22] to produce linear plots from

which $v_2$ was calculated:

$$v = (v_2 - v_0)\omega_2 + v_0 \qquad (14)$$

where:

$v$ = specific volume of solution;
$v_0$ = specific volume of solvent mixture;
$v_2$ = partial specific volume of polymer.

As the volume fraction of TFAA in the solvent mixture increases, the partial specific volume of LCP decreases (*Figure 7*).

*Molecular weights and second virial coefficients*

Evaluation of the true values of both molecular weight ($M_w$) and second virial coefficient ($A_2$) for a possibly rod-like polymer in a mixed solvent necessitates a knowledge of the molecular anisotropy factor, $\delta$, and the s.r.i.i. at constant chemical potential, $v_\mu$. Equation (1) is the relevant equation for evaluation of $M_w$ and $A_2$. Measurements of the horizontal and vertical components of the excess scattered light intensity, $R_{HV}$ and $R_{VV}$, were made in the KMX-6 photometer using the analyser attachment with the instrument. For all solutions of all fractions, $R_{HV}$ was found to be zero and hence $\delta = 0$, i.e. there appears to be no molecular anisotropy of LCP in the TFA/DCM solvent mixture. Consequently, there was no need to apply the corrections described by Berry and others which were discussed earlier. The values of the true molecular weight and second virial coefficient ($A_2$) for each fraction in each solvent mixture are given in *Table 1*. The dependence of $A_2$ on solvent composition was qualitatively similar for all fractions and is shown in *Figure 8* for fractions LCP1, LCP5 and LCP9 respectively. Initially the values of $A_2$ decrease as $\phi_{TFA}$ increases and a minimum is obtained at $\phi_{TFA} \simeq 0.35$. Thereafter $A_2$ increases again.

## DISCUSSION

*Unperturbed dimensions and polymer–solvent interaction parameter*

For rigid rod molecules Zimm[23] derived equation (15) below relating $A_2$ to $M_w$ and the rod length $L$:

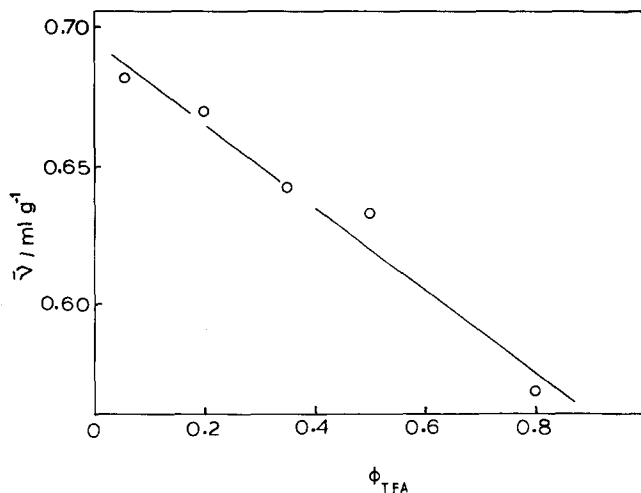$$A_2 = \pi N_A D L^2 / 4 M_w^2 \qquad (15)$$



**Figure 7** Variation of partial specific volume of LCP with volume fraction of TFA

**Table 1** Molecular weights and second virial coefficients of LCP fractions in TFA/DCM mixes at 25°C

| | $\phi_{TFA}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.05 | 0.2 | 0.35 | 0.5 | 0.67 | 0.8 | Average $M_w/10^3$ |
| *Molecular weights* $(10^3 \text{ g mol}^{-1})$ | | | | | | | |
| LCP1 | 149.5 | 158.7 | 145.4 | 146.4 | 139.0 | 142.3 | 146.9 |
| LCP2 | 140.1 | 132.3 | 123.8 | 119.0 | 124.0 | 126.9 | 127.7 |
| LCP3 | 101.5 | 86.6 | 105.7 | 107.1 | 103.5 | 93.8 | 99.7 |
| LCP4 | 99.5 | 99.5 | 100.4 | 100.1 | 98.7 | 105.4 | 100.6 |
| LCP5 | 92.1 | 97.2 | 77.5 | 70.5 | 91.0 | 88.4 | 86.1 |
| LCP6 | 69.1 | 82.8 | 64.6 | 65.3 | 64.8 | 75.5 | 70.4 |
| LCP7 | 55.2 | 52.6 | 54.0 | 55.1 | 53.2 | 51.5 | 53.6 |
| LCP8 | 49.7 | 45.3 | 33.2 | 44.7 | 47.0 | 47.0 | 44.5 |
| LCP9 | 10.4 | 10.5 | 8.0 | 8.0 | 9.5 | 8.7 | 9.2 |
| *Second virial coefficients* $(10^{-4} \text{ ml mol g}^{-2})$ | | | | | | | |
| LCP1 | 6.1 | 5.6 | 5.4 | 6.1 | 6.9 | 7.6 | |
| LCP2 | 6.2 | 5.7 | 5.5 | 6.1 | 6.9 | 7.7 | |
| LCP3 | 6.4 | 5.9 | 5.7 | 6.4 | 7.1 | 8.0 | |
| LCP4 | 6.9$_7$ | 5.9$_8$ | 5.8 | 6.8 | 7.1 | 8.2 | |
| LCP5 | 6.7 | 6.2 | 6.0 | 6.7 | 7.6 | 8.4 | |
| LCP6 | 7.0 | 6.5 | 6.3 | 7.0 | 7.8 | 8.3 | |
| LCP7 | 7.4 | 6.8 | 6.6 | 7.3 | 8.2 | 8.9$_6$ | |
| LCP8 | 7.7 | 7.1 | 6.9 | 7.6 | 8.7 | 9.1 | |
| LCP9 | 7.4 | 6.6 | 6.2 | 6.5 | 7.5 | 8.5 | |
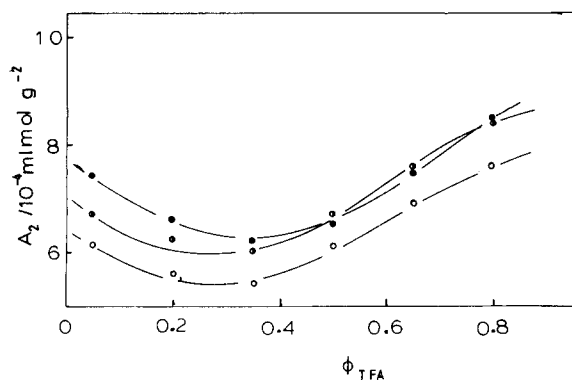


**Figure 8** Variation of second virial coefficient variation with volume fraction of TFA: O, fraction LCP1; ◑, fraction LCP5; ●, fraction LCP9

where $N_A$ = Avogadro's number and $D$ = rod diameter. For Gaussian coil molecules the relation between $A_2$ and $M_w$ can be generally written as

$$A_2 = A_0 M_w^{-\alpha} \qquad (16)$$

where the values of 0.25 or 0.15 have been attributed to $\alpha^{24}$. Equation (15) indicates no dependence of $A_2$ on $M_w$ for truly rigid-rod molecules since $L \propto M_w$. Double logarithmic plots of $A_2$ as a function of $M_w$ were linear for all the solvent compositions used. Values of $\alpha$ in equation (16) for $\phi_{TFA} = 0.35$, 0.50 and 0.80 were 0.25$_7$, 0.18$_9$ and 0.15$_3$, respectively. These exponents suggest that the LCP investigated here has a coil-like conformation in dilute solution. The values of $A_2$ and $M_w$ were utilized in a Kurata plot$^{25}$ (equation (17)) to estimate the unperturbed dimensions of the polymer. *Figure 9* shows the data for all solvent mixtures plotted according to equation (17), the line being a linear least squares fit to the data:

$$A_2 M_w^{1/2} = 1.65 \times 10^{23} A^3 + 0.968 \times 10^{23} B M_w^{1/2} \qquad (17)$$

where $A = (\langle r^2 \rangle_0/M)^{1/2}$ and $\langle r^2 \rangle$ = mean square unperturbed end-to-end distance. Values of $A$ and $B$
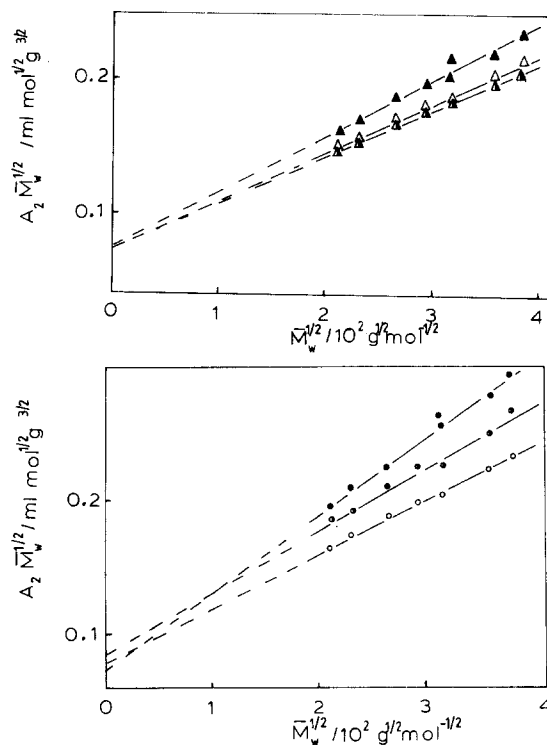


**Figure 9** Kurata plots for LCP fractions in TFA/DCM mixtures for various $\phi_{TFA}$ values: △, 0.2; ▲, 0.35; ▲, 0.5; O, 0.05; ◑, 0.658; ●, 0.8

obtained are given in *Table 2*. The values of $A$ in each TFA/DCM mixture are remarkably constant, indicating the absence of any specific solvent effects, notwithstanding the change in polarity of the solvent medium over the range of solvent mixtures used. The average value of $A$ obtained is $7.72 \times 10^{-9}$ cm*. To our knowledge, the only other main chain aromatic polyester for which

* Although the LCP was fractionated, it was impossible to make osmometric measurements in the TFA/DCM mixed solvent due to the gradual dissolution and eventual fragmentation in the cellulose membrane. Consequently the value of $A$ obtained here is strictly $(\langle r^2 \rangle_0/M_w)^{1/4}$

**Table 2** Values of $A$ and $B$ parameters from Kurata plots for LCP in TFA/DCM mixtures

| $\phi_{TFA}$ | $A$ ($10^{-9}$ cm) | $B$ ($10^{-27}$ cm$^3$ mol$^2$ g$^{-2}$) |
|---|---|---|
| 0.05 | 7.84 | 4.13 |
| 0.20 | 7.62 | 3.78 |
| 0.35 | 7.63 | 3.57 |
| 0.50 | 7.62 | 4.34 |
| 0.65 | 8.02 | 4.70 |
| 0.80 | 7.61 | 5.93 |
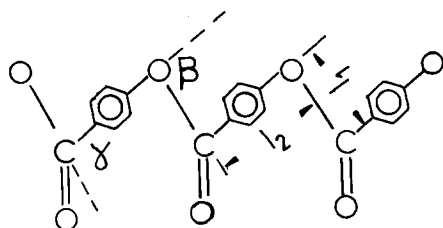
**Figure 10** Idealized chain structure of poly $p$-hydroxybenzoic acid

values of $A$ (or characteristic ratio, $C_\infty$) have been reported, is polyethylene terephthalate. Wallach[26] quotes a value of $\approx 10 \times 10^{-9}$ cm obtained from viscometry data, which agrees with rotational isomeric state calculations of Williams and Flory[27], who obtained $A = 9.6 \times 10^{-9}$ cm. Flory[28] comments that this is a low value and probably arises from the planar *trans* ester groups imparting enhanced rotational freedom to adjoining bonds. With the terpolymer LCP, we cannot unambiguously define the repeat unit and hence obtain a value for the characteristic ratio ($C_\infty$) to compare with others. Neither can we calculate a value for the free rotation dimensions of the molecule in a simple manner, again because of the ambiguous nature of the repeat unit and consequently the variation in bond angles and lengths. However, a value for the free rotation dimensions of poly $p$-hydroxy benzoic acid can be calculated using the procedure outlined by Huglin and Stepto[29]. An idealized chain structure for this polymer is shown in *Figure 10*, which corresponds to the situation where $M = 1$ in Huglin and Stepto's notation. Valence angles $\beta$ and $\gamma$ together with bond lengths $l_1$ and $l_2$ were optimized using a molecular orbital calculation for a chain fragment consisting of three HBA units. These values were inserted into the relevant expressions and the ratio $(\langle r^2 \rangle_{0f}/N)^{1/2}$ calculated as a function of number of bonds, $N$, in the chain (*Figure 11*). For an infinitely long chain the value of $(\langle r^2 \rangle_{0f}/M)^{1/2}$ obtained from these calculations is $3.68 \times 10^{-9}$ cm. For a polymer consisting of alternating HQ and IPA residues, such a straightforward calculation is not possible due to the *meta* linkage on the IPA residue. Furthermore, there are at least three different bond lengths and three valence angles to consider. Therefore, we can only tentatively suggest that the steric hindrance factor, $\sigma^2$, for LCP obtained from $\langle r^2 \rangle_0 / \langle r^2 \rangle_{0f}$ is $\approx 4.4$. This is a high value in comparison to other (aliphatic) condensation polymers, and is in the region of values quoted for cellulose derivatives.

The parameter $B$ obtained from the slope of the Kurata plot is related to the binary cluster integral, $\beta$ (Reference 30), via the relation

$$B = \beta / M_s^2 \tag{18}$$

where $M_s$ = segment molecular weight. The binary cluster integral may be written in terms of the Flory polymer–solvent interaction parameter, $\chi$, as

$$\beta = \frac{2M^2 v_2^2}{N_A n^2 V_1} (\tfrac{1}{2} - \chi) \tag{19}$$

where $n$ = the number of segments in a polymer chain of total molecular weight $M$ and $V_1$ = molar volume of solvent. Hence

$$B = (2\bar{v}_2^2/N_A V_1)(\tfrac{1}{2} - \chi) \tag{20}$$

The value of $B$ is determined by the thermodynamic quality of the solvent for the polymer, a value of zero being equivalent to a theta solvent[30]. Consequently, the values of $B$ should have the same qualitative behaviour as $A_2$. Inspection of the values of $B$ in *Table 2* confirms this in that, as $\phi_{TFA}$ increases, $B$ decreases to a minimum at $\phi_{TFA} = 0.35$ before increasing again. Values of $\chi$ have been calculated using the values of $B$ in *Table 2* and partial specific volumes of LCP. Molar volumes of the solvent mixtures were calculated as the mole fraction weighted sum of the molar volumes of the solvent components. *Figure 12* shows the variation of the polymer–solvent interaction parameter so obtained with
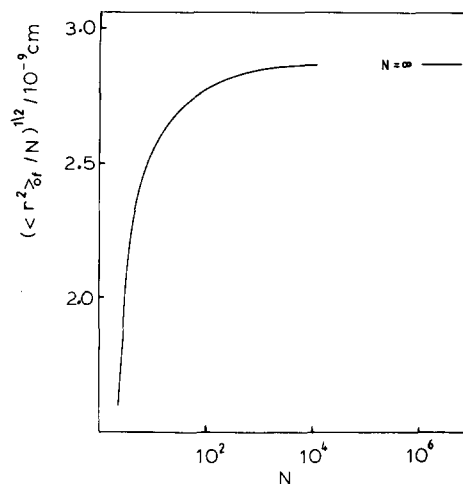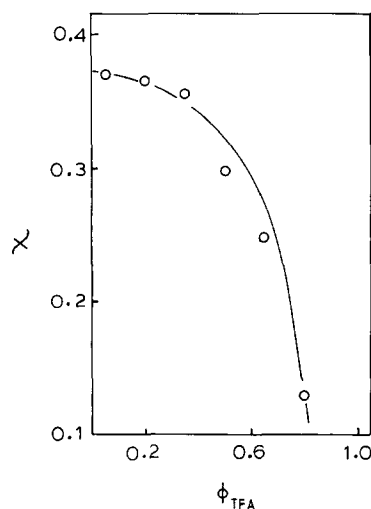
**Figure 11** Values of $(\langle r^2 \rangle_{0f}/N)^{1/2}$ calculated for poly $p$-hydroxybenzoic acid as a function of the number of bonds in the chain

**Figure 12** Polymer–solvent interaction parameter, $\chi$, calculated from slopes of Kurata plots as a function of volume fraction of TFA in the mixed solvent

**Table 3** Excess number of TFA molecules, $n_{TFA}$, and number of TFA molecules per monomer unit of LCP

| $\phi_{TFA}$ | $\alpha_{TFA}$ (ml g$^{-1}$) | $n_{TFA}$ | Number of molecules |
|---|---|---|---|
| 0.05 | 0.33 | 600 | 0.7 |
| 0.2 | 0.45 | 893 | 1.1 |
| 0.35 | 0.77 | 1430 | 1.7 |
| 0.50 | 0.74 | 1284 | 1.5 |
| 0.65 | 0.59 | 957 | 1.1 |
| 0.80 | 0.51 | 765 | 0.9 |

volume fraction of trifluoroacetic acid. The values suggest that the solvent is, thermodynamically, a very good solvent for LCP, becoming better as the TFA composition increases. This agrees, qualitatively, with the observation that TFA is preferentially adsorbed on to the molecule.

*Preferential adsorption parameter*

In other co-solvent systems, a characteristic feature of the preferential adsorption parameter, $\alpha$, has been the occurrence of initially positive values of $\alpha$ changing to strongly negative values at higher volume fractions of solvent 1. This behaviour is not observed here, $\alpha_{TFA}$ being large and positive over the whole range of TFA content investigated. The values of $\alpha_{TFA}$ can be used to gain more insight into the nature of polymer–solvent interaction. Strazielle and Benoit[31] view the polymer molecule in a mixed solvent as enclosed in a sphere whose molecular composition differs from the solvent composition in the absence of preferential adsorption by excess quantities $n_1$ and $n_2$ (both 1 and 2 being low molecular weight solvents). It can be shown that

$$\alpha_1 = n_1 V_1/M_w \tag{21}$$

where $V_1$ is the partial molar volume of solvent 1.

Values of $v_{TFA}$ were calculated using the density data of the TFA/DCM mixtures plotted in *Figure 2* by the method of intercepts. These values were then used to calculate the variation of $n_{TFA}$ with solvent composition. *Table 3* shows the values of $n_{TFA}$ obtained and the number of TFA molecules per monomer residue. For this purpose the average segment molecular weight was calculated as the composition weighted sum of the molecular weights of the HBA, HQ and IPA components. We have not differentiated between the monomer residues thus far, but it appears most likely that TFA hydrogen bonds to the relatively electronegative carbonyl groups in the polymer.

In principle, it should be possible to relate the preferential adsorption coefficient to the various interaction parameters in the polymer–solvent system. Read[22] has discussed this with respect to polystyrene dissolved in cyclohexane–benzene mixtures. However, even in this system where only dispersion forces predominate, there has been some argument as to the need to include ternary interaction parameters ($\chi_{123}$, $\chi_{133}$, $\chi_{233}$, where 1 and 2 refer to solvent and 3 refers to polymer). For the polar and hydrogen bonded TFA/DCM mixture used here, additional ternary interaction parameters describing possible solvent–solvent interactions are required, and the total number of interaction parameters needed increases to seven. The possibility of non-linear least squares fitting of the theoretical equation to the six values of $\alpha_{TFA}$ therefore becomes invalid. If estimates for the

solvent–solvent interaction parameters were available, this would reduce the number of adjustable fitting parameters ($\chi$ values) to make such a procedure possible. Interaction parameters for the solvent pair alone are obtainable from the excess Gibbs free energy of mixing of the solvent components. The latter function is obtainable[33] from light scattering data on the solvent mixture using the relation

$$(1 - R_{id}/R_c) = \Delta G^E/RT \tag{22}$$

where $R_{id}$ = ideal Rayleigh ratio for the mixture and $R_c$ = Rayleigh ratio due to concentration fluctuations.

As *Figure 13* shows, the isotropic Rayleigh ratio ($R_{is}$) for TFA/DCM mixtures is highly non-ideal. The values of $R_c$ are the difference between $R_{is}$ and the density fluctuation contribution to the scattering ($R_d$). This latter quantity is calculable from a formula due to Einstein[34], but regrettably this requires values for the isothermal compressibility of the two pure liquids. Although the isothermal compressibility for DCM is available, no value could be found for TFA. Consequently, further attempts at the thermodynamic interpretation of $\alpha$ were prevented.

CONCLUSIONS

Although the main chain aromatic polyester contains a high proportion of rigid groups in its backbone, no evidence for molecular anisotropy was found in trifluoroacetic acid/dichloromethane solutions. Furthermore, the dependence of true second virial coefficient on true molecular weight was akin to that expected for a random coil molecule. Values for the unperturbed dimensions obtained from Kurata plots are less than reported values for polyethylene terephthalate and much less than a value calculated for a semi-rigid rod polymer. A tentative calculation of the steric hindrance factor to free rotation suggests that this is high.

Although the solvent system used is an example of a co-solvent system, the polymer–solvent interaction parameters calculated show that the combination is thermodynamically a very good solvent. From optical measurements on the solutions it has been shown that the trifluoroacetic acid is preferentially adsorbed into the region of the polymer. Attempts at thermodynamic interpretation of the preferential adsorption coefficient were frustrated by the lack of thermodynamic data for the trifluoroacetic acid.
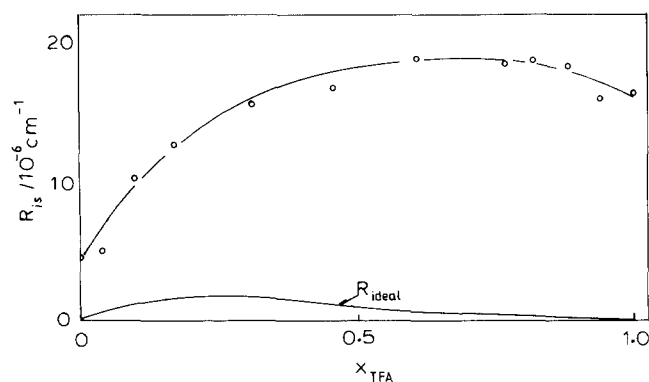


**Figure 13** Isotropic Rayleigh ratio, $R_{is}$, as a function of TFA molefraction, $x_{TFA}$: $\bigcirc$, measured data (from low angle laser light scattering, $\lambda_0 = 632.8$ nm)[35]; ———, calculated ideal scattering

## ACKNOWLEDGEMENTS

## REFERENCES

1    Ciferri, A., Krigbaum, W. R. and Meyer, R. B. 'Polymer Liquid Crystals', Academic Press, London, 1982
2    'Polymer Liquid Crystals' *Farad. Discuss. Chem. Soc.* 1985, no. 79
3    Ying, Q., Chu, B., Qian, R., Bao, J., Zhang, J. and Xu, C. *Polymer* 1985, **26**, 1401
4    Arpin, M. and Strazielle, C. *Polymer* 1977, **18**, 591
5    Lee, C. C., Chu, S-G. and Berry, G. C. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1573
6    Krigbaum, W. R. and Tanaka, T. *Macromolecules* 1988, **21**, 743
7    Krigbaum, W. R. and Brelsford, G. *Macromolecules* 1988, **21**, 2502
8    Berry, G. G. *J. Polym. Sci. Polym. Symp.* 1978, **65**, 143
9    Bushuk, W. and Benoit, H. *Can. J. Chem.* 1960, **57**, 524
10   Kratochvil, P., Sedlacek, B., Strakova, D. and Tuzar, Z. *Makromol. Chem.* 1971, **148**, 271
11   Tuzar, Z., Kratochvil, P. and Strakova, D. *Eur. Polym. J.* 1970, **6**, 1113
12   Huglin, M. B. and Richards, R. W. *J. Appl. Polym. Sci.* 1980, **25**, 2513
13   Kambe, H., Kambe, Y. and Honda, C. *Polymer* 1973, **14**, 460
14   Huglin, M. B. 'Light Scattering from Polymer Solutions', (Ed. M. B. Huglin), Academic Press, London, 1972, ch. 6
15   Stockmayer, W. H. and Chan, L.-L. *J. Polym. Sci. A2* 1966, **4**, 437
16   Kaye, W. *Anal. Chem.* 1973, **45**, 221A
17   van Krevelen, D. W. and Hoftyzer, P. J. 'Properties of Polymers', Elsevier, 1976
18   Eisenlohr, F. *Z. Phys. Chem.* 1910, **A75**, 585
19   Ooi, T. *J. Polym. Sci.* 1958, **28**, 459
20   Cowie, J. M. G. *Pure Appl. Chem.* 1970, **23**, 355
21   Strazielle, C. in 'Light Scattering from Polymer Solutions' (Ed. M. B. Huglin), Academic Press, London, 1972, ch. 15
22   Klarner, P. E. O. and Ende, H. A. 'Polymer Handbook' (Ed. J. Brandrup and E. H. Immergut), 2nd Edn, Wiley, New York, 1975, p. IV 61
23   Zimm, B. H. *J. Chem. Phys.* 1946, **14**, 164
24   Kurata, M. and Stockmayer, W. H. *Fortsch. Hochpolym. Forsch.* 1963, **3**, 196
25   Kurata, M., Fukatsu, M., Sotobayashi, H. and Yamakawa, H. *J. Chem. Phys.* 1964, **41**, 139
26   Wallach, M. L. *Makromol. Chem.* 1967, **103**, 19
27   Williams, A. D. and Flory, P. J. *J. Polym. Sci. A–2* 1967, **5**, 417
28   Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley Interscience, New York, 1969
29   Huglin, M. B. and Stepto, R. F. T. *Makromol. Chem.* 1970, **132**, 225
30   Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
31   Strazielle, C. and Benoit, H. *J. Chem. Phys.* 1961, **59**, 675
32   Read, B. E. *Trans. Faraday Soc.* 1960, **56**, 382
33   Coumou, D. J. and Mackor, E. L. *Trans. Faraday Soc.* 1964, **60**, 1726
34   Einstein, A. *Ann. Phys.* 1910, **33**, 1275
35   Values of $R_{150}$ for the TFA/DCM mixtures were obtained from low angle laser light scattering data using the KMX6 photometer and calculation of the Cabannes factor from measurements of the depolarized scattering intensity using the analyser facility on the instrument