BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 14, pp. 2773–2780, 1995

0032-3861/95/$10.00+0.00

Configurational changes in precursor polymers of poly(*p*-phenylene)

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(Received 13 December 1994)

Intrinsic viscosity and light scattering measurements have been made on dilute solutions of partially aromatized precursor polymers of poly(*p*-phenylene) in *N*-methylpyrrolidinone. These data have been used to provide values of the persistence length and shift factor in the worm-like-chain model of semiflexible molecules. Because of aggregation effects, interpretation of the data has been restricted to a maximum of 20% aromatization. Viscosity data indicate that persistence lengths increase from ca. 12 to 130 Å as the percentage aromatization increases from 0 to 20%. The shift factor also increases over this range. Light scattering values for the radius of gyration also produce persistence length values which increase with percentage aromatization but the values are larger than the viscometric values. Light scattering data are more scattered than viscosity data and possible sources for this disparity are discussed.

(Keywords: poly(*p*-phenylene); precursor polymer; configuration)

INTRODUCTION

Poly(*p*-phenylene) (PPP) is a polymer which has several attractive properties. The absence of coupling groups between the phenylene rings makes the polymer less susceptible, in principle, to degradation by thermal or chemical attack. A high degree of conjugation is exhibited by the polymer and doping can increase the conductivity from that of an insulator to that of a semiconductor. Since the polymer has no substituents and is anticipated to have a linear rod-like molecular configuration, a high degree of crystallinity would therefore be expected. However, there has been yet no successful method of direct synthesis of the material with a high degree of polymerization[1,2]. Oligomeric materials are usually obtained which are insoluble and for which degradation intervenes before the crystalline melting point is observed. A strategy which has been adopted to obtain PPP is to synthesize a precursor polymer which is then subsequently treated to produce the desired material[3,4]. A favoured route has been the polymerization of disubstituted cyclohexadienes which on pyrolysis produce PPP. The disubstituted cyclohexadiene monomer has been produced both via conventional synthetic routes and by the bacterial oxidation of benzene.

The pyrolysis reaction is base catalysed but full aromatization generally yields oligomeric material with ca. 7 to 20 phenylene units, depending on whether the aromatization is performed on the solid polymer or in solution[5]. This degradation in molecular weight has been attributed to the occurrence of 1,2-addition, to the extent of 15% of the main chain bonds in the poly(cyclohexadiene) precursor polymer. Such 1,2-addition leads to kinks in the molecule which were thought to become sufficiently strained when neighbouring groups are aromatized that bond rupture ensues. Recently[6,7], the synthesis of a wholly linear poly(cyclohexadiene) precursor molecule has been reported, but this molecule is even more susceptible to degradative rupture than the polymer with 1,2-addition. Not withstanding these aspects of the pyrolysis of the precursor molecule, it is found that conversion to PPP does not proceed at a regular rate but takes place by an autocatalytic reaction[8]. Additionally, as our earlier size exclusion results[8] have demonstrated, aromatization leads not only to a reduction in molecular weight but also to the molecular-weight distribution becoming increasingly bimodal as aromatization progresses. Both high- and low-molecular-weight portions of this bimodal distribution have the same degree of aromatization. It is believed that the high-molecular-weight portion of the distribution is due to sequences of *p*-phenylene units up to 20 units in length on different molecules aggregating together, with the lower-molecular-weight portion having *p*-phenylene units distributed at random along the molecules.

We report here the use of viscometry and intensity light scattering on dilute solutions in *N*-methylpyrrolidinone of the precursor polymer and the polymer produced with aromatization of up to ca. 30%. The main objective of this work was to ascertain whether the partial aromatization led to a gradual stiffening of the

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molecule and for this reason we have obtained values of the persistence length as a function of percentage aromatization.

THEORY

The configurational statistics of flexible polymer molecules are describable by using a Gaussian segment density distribution about the centre of mass[9]. Experimental investigations over the past 40 years have confirmed that the essential features of this model are valid for many polymers, whether in dilute solution or the bulk amorphous melt[10,11]. Similarly, a molecule which is a true thin narrow rod can also be described accurately from a configurational viewpoint[10]. However, a complete description of the configuration of molecules which have mixed flexible/rigid-rod character, i.e. semiflexible molecules, can lead to complicated expressions[12]. A frequently adopted model is the worm-like chain or Kratky–Porod chain, named after the original introducers of the model[13,14].

A worm-like chain is modelled by a freely rotating chain of N bonds of length l with a supplementary bond angle of ϕ. In the absence of excluded volume interactions, the worm-like chain is obtained from this freely rotating model in the limit as N tends to infinity with both l and ϕ tending to zero, but the approaches to these limiting conditions are such that the following apply:

$$L = \lim_{\substack{N \to \infty \\ l \to 0}} N/l \tag{1}$$

and

$$a = \lim_{\substack{\phi \to 0 \\ l \to 0}} l/(1 - \cos\phi) \tag{2}$$

and both L and a remain finite. In these relationships, L is the contour length and a the persistence length of the worm-like chain, and these two parameters are sufficient to quantify the model. The mean square end-to-end distance $\langle r^2 \rangle$ and mean square radius of gyration $\langle s^2 \rangle$ for a worm-like chain are given by the following:

$$\langle r^2 \rangle = 2aL - 2a^2(1 - \exp(-L/a)) \tag{3}$$

and

$$\langle s^2 \rangle = \frac{aL}{3} - a^2 + (2a^3/L)\{1 - (a/L)[1 - \exp(-L/a)]\} \tag{4}$$

As the persistence length takes on larger values, the chain becomes more extended in the direction of the vector which is tangential to the end of the molecule. As $(L/a) \to \infty$:

$$\langle r^2 \rangle = 6\langle s^2 \rangle = 2La \tag{5}$$

and as $(L/a) \to 0$:

$$\langle r^2 \rangle = 12\langle s^2 \rangle = L^2 \tag{6}$$

These last two equations show that the worm-like chain recovers Gaussian behaviour for an infinitely long chain but displays rigid-rod-like behaviour as either the molecule becomes shorter or the persistence length increases. Between these two limits, the worm-like chain can take on a variety of configurations depending on the magnitude of the persistence length.

Another model of macromolecules which has aspects of rod-like nature is to describe them as a thin wire[15] and the stiffness of the molecule is characterized by the magnitude of the bending energy per unit contour length as a result of the deviation from a straight rod-like configuration. In this model this force constant α_0, for a bend of the molecule is given by the following:

$$\alpha_0 = aK_B T \tag{7}$$

where K_B is Boltzmann's constant.

Hence again the persistence length is an important parameter in the quantitative description of the molecule. As a increases, the molecule becomes increasingly resistant to any distortions away from a linear path.

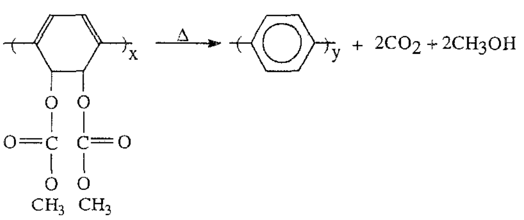
Yamakawa and coworkers[12,16] have elaborated the worm-like chain to the helical worm-like chain model wherein the molecule also stores torsional energy as well as bending energy. Although static and dynamic properties of this latter model have been calculated theoretically, many more parameters are required to describe such a molecule and a full experimental examination of this model has yet to be attempted. We confine our attention here to the use of the worm-like chain and restrict our attention to the evaluation of the persistence length and the shift factor M_L which is related to the contour length by the relationship $M_L = \bar{M}_w/L$, and thus has a characteristic value for the polymer, which is independent of molecular weight.

EXPERIMENTAL

Precursor polymer preparation

The monomer for the preparation of the precursor polymer was 5,6-*cis*-dimethylcarboxycyclohexa-1,3-diene (DHCDDMC) and its preparation and polymerization, plus fractionation of the resultant polymer, have been described earlier[8]. Nine fractions of the unaromatized polymer (poly(DHCDDMC)) were obtained, covering a range in molecular weight from 1×10^5 to 1.22×10^6 g mol^{-1}. Solutions of these fractions were made in N-methylpyrrolidinone (NMP) at ca. 5% w/v and heated in a nitrogen atmosphere at 448 K for varying times. The extent of aromatization was calculated from the volume of carbon dioxide gas evolved in the reaction shown in *Scheme 1*.

The details of this procedure have been given earlier[8]. Because of the degradation reactions referred to above, the degrees of polymerization (x and y) are not equal and there is a loss of molecular weight ordering of the fractions due to the random nature of the aromatization reaction. Each partially aromatized fraction was isolated by pouring the NMP solution into methanol and filtering



Scheme 1

Table 1 Partial specific volume ($\bar{v}_2$) and specific refractive index increments (ν) for partially aromatized polymers in NMP solutions at 297 K

Amount of aromatization (%)	$\bar{v}_2$ (ml g^{-1})	ν (ml g^{-1})
0	0.749	0.060
10	0.744	0.090
20	0.818	0.139
30	0.801	0.180
40	0.722	0.206

off the precipitate, followed by washing with methanol and drying to constant weight under vacuum. These fractions were stored in a freezer until required. The maximum extent of aromatization investigated here was 40%.

Partial specific volumes, refractive indices and specific refractive index increments

Classical intensity light scattering (CILS) and intrinsic viscosity data were obtained for solutions of the unaromatized and aromatized polymers in NMP only. Interpretation of these data required complementary parameters to be available.

Partial specific volumes of the polymers were determined using an Anton Paar DMA601 digital densitometer and associated DMA60 controller. All measurements were made at 298 K and the solutions were made up in vacuum degassed NMP. The concentration range of the solutions used to obtain the partial specific volumes was from 1 to 5% w/v and the densities obtained were accurate to $\pm 0.0008\ \mathrm{g\,mol^{-1}}$, as estimated from repeated measurements. The data were plotted according to the following relationship:

$$\rho_s^{-1} = w(\bar{v}_2 + \rho_0^{-1}) - \rho_0^{-1}$$

where ρ_s is the solution density, ρ_0 the density of the pure solvent, w the weight fraction and $\bar{v}_2$ the partial specific volume of the polymer. Thus the partial specific volume is obtained from the slope of a plot of ρ_s^{-1} as a function of w. Values of $\bar{v}_2$ obtained for each percentage aromatization are given in *Table 1*.

The refractive index ($\tilde{n}_0$) of NMP was obtained for a light wavelength of 488 nm by interpolating values obtained at wavelengths of 404.7, 435.8, 546.1, 579.1 and 589.0 nm: for this interpolation the refractive indices were plotted according to a Cauchy dispersion formula ($\tilde{n}_0$ as a function of λ_0^{-2} where λ_0 is the vacuum wavelength of the light). Refractive indices were obtained using a Pulfrich refractometer, and at an NMP temperature of 298 K the refractive index obtained at 488 nm was 1.4775. Specific refractive index increments (*SRII*s) at 488 nm of the poly(DHCDDMC) and the partially aromatized polymers were obtained by using a Wyatt Optilab 903 refractometer. Data were plotted as $\Delta n/c$ as a function of the concentration c (Δn is the refractive index difference between solvent and solution) and ν, the *SRII*, was obtained as the intercept in such a plot. *Table 1* reports the values of ν obtained in NMP at 298 K.

Classical intensity light scattering

All CILS data were obtained at 298 K by using a Malvern 4700 photon correlation spectrometer. The goniometer was mounted on an Ealing gas-damped optical table and an argon ion laser with a wavelength of 488 nm was used as a light source. Before use the laser and other optical components were precisely aligned so that the normalized scattered light intensity from toluene over the scattering angle range from 30 to 150° was 1 ± 0.05 when ratioed to the intensity of light scattered at 90°. Toluene was used as the primary calibrant to convert photomultiplier output to absolute Rayleigh ratio. A value[17] of $31.0 \times 10^{-6}\ \mathrm{cm^{-1}}$ was used as the absolute Rayleigh ratio of toluene at 488 nm and 298 K. Solutions of the partially aromatized polymers were made up in freshly distilled solvent and left to dissolve for 24 h. Each solution was then repeatedly filtered through poly(tetrafluoroethylene) membrane filters which had a pore diameter of 0.2 μm, with the final filtering being directly into a high quality light scattering cell. Scattered light intensities were measured over an angular range between 30 and 150° to the incident beam direction, at 10° intervals.

Dilute solution viscometry

Intrinsic viscosities of the partially aromatized polymer in NMP solution were obtained by using an Ubbelohde suspended level viscometer fitted with an internal glass filter. This viscometer was sealed from the atmosphere by fitting an aspirating apparatus to the ground glass joints of the viscometer limbs so that the contents of the viscometer were never contacted by moist air. The viscometer was first flushed with dry nitrogen before a known volume of a ca. 1.0% w/v solution of the polymer was placed into it. Dilutions were made *in situ* with the solution being mixed by gently bubbling in dry nitrogen. Measurements of the flow times of the solution were repeated until two consecutive timings were within ±0.05 s of each other.

RESULTS

Light scattering

Typical Zimm plots for poly(DHCDDMC) and the partially aromatized polymer are shown in *Figure 1*. Values of the weight-average molecular weight ($\bar{M}_w$), the z-average mean square radius of gyration ($\langle s^2\rangle_z$) and the second virial coefficient (A_2) were obtained by conventional extrapolation procedures. The weight-average mean square radius of gyration, $\langle s^2\rangle_w$, was obtained by correction of the $\langle s^2\rangle_z$ values using the following relationship[18]:

$$\langle s^2\rangle_w = \langle s^2\rangle_w\left(\frac{h+1}{h+2}\right) \tag{8}$$

and

$$h = \left(\frac{\bar{M}_w}{\bar{M}_n} - 1\right)^{-1} \tag{9}$$

Figure 2 shows a double logarithmic plot of $\langle s^2\rangle_w$ as a function of $\bar{M}_w$ for the unaromatized polymer; the linear least-squares fit to these data is given by the following relationship:

$$\langle s^2\rangle_w = 0.065\bar{M}_w^{1.15} \tag{10}$$

Least-squares fitting to a double logarithmic plot of the second virial coefficients as a function of molecular

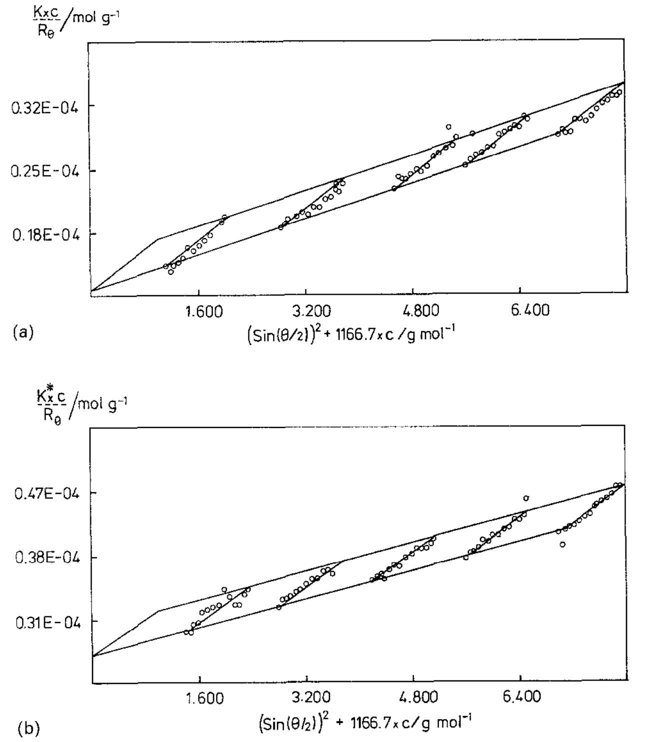


Figure 1 Zimm plots for DHCDDMC polymer in NMP solution: (a) % aromatized, molecular weight = 77.6 × 10^3; (b) 20% aromatized, molecular weight = 44.0 × 10^3

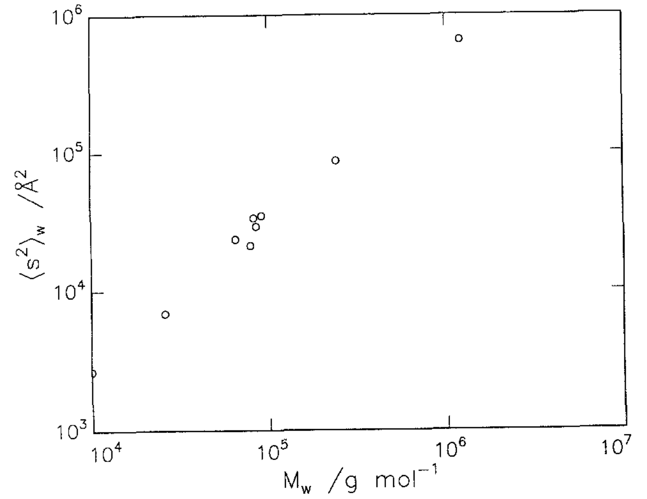


Figure 2 Double logarithmic plot of weight-average mean square radius of gyration as a function of molecular weight for the unaromatized polymer

weight gives the following:

$$A_2 = 8.6 \times 10^{-3} \bar{M}_w^{-0.16} \tag{11}$$

Aromatization is accompanied by an initial fall in molecular weight which is much greater than that calculated from the stoichiometry of the aromatization reaction, and the molecular weights tend to 'bunch'. *Figures 3a* and *3b* illustrate this bunching in plots of the mean square radius of gyration as a function of the molecular weight. For the 30 and 40% aromatized copolymers, the bimodality of the molecular weight distribution is marked, and so consequently we have not attempted to correct the *z*-average radii of gyration to weight-average values. Our previous size exclusion chromatography investigations of the partially aromatized polymer showed that as aromatization proceeds the molecular weight distributions became more bimodal[8]. Additionally, the initial reduction in molecular weight eventually transforms to an increase in molecular weight as aromatization proceeds. This same behaviour is observed in the molecular weights obtained by light scattering. Generally, as the degree of aromatization increased, the second virial coefficient decreased, i.e. NMP became thermodynamically less favourable as a solvent. Because of the bunching of the molecular weights, and the increased scatter of the values of $\langle s^2 \rangle_z$ for 30 and 40% aromatization and the knowledge that bimodal molecular weight distributions exist in these two latter polymers, empirical relationships between molecular weight and $\langle s^2 \rangle_w$ have only been obtained for 10 and 20% aromatization, as follows:

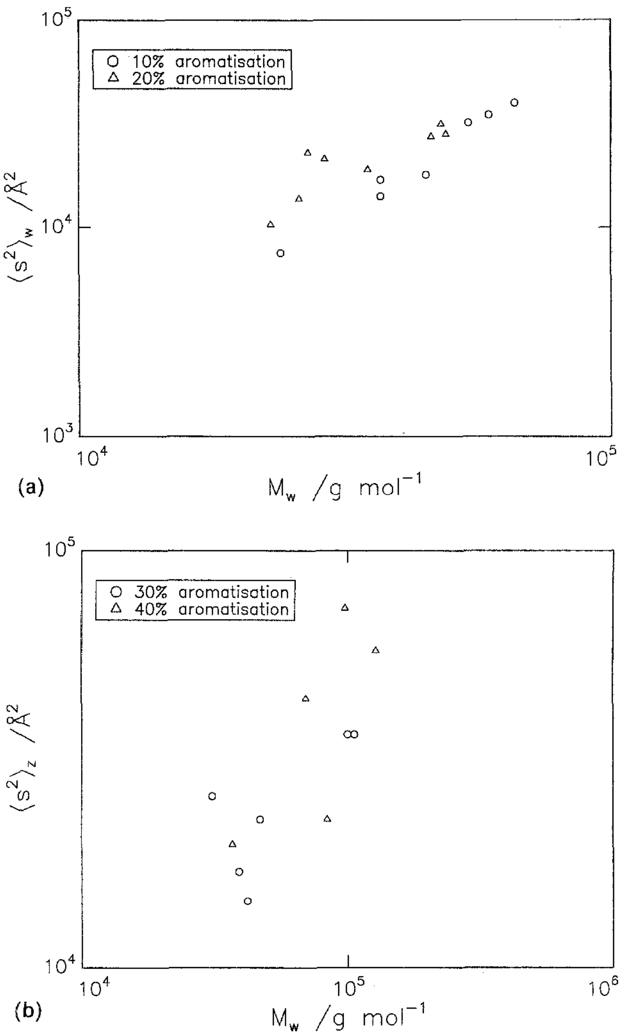


Figure 3 Double logarithmic plots of the mean square radius of gyration as a function of molecular weight for: (a) 10 and 20% aromatization (weight-average values); (b) 30 and 40% aromatization (z-average values)

$$10\% \ \langle s^2 \rangle_w = 1.9 \times 10^{-4} \bar{M}_w^{1.76} \tag{12}$$

$$20\% \ \langle s^2 \rangle_w = 4.3 \times 10^{-3} \bar{M}_w^{1.5} \tag{13}$$

Intrinsic viscosity

Intrinsic viscosity values for the partially aromatized

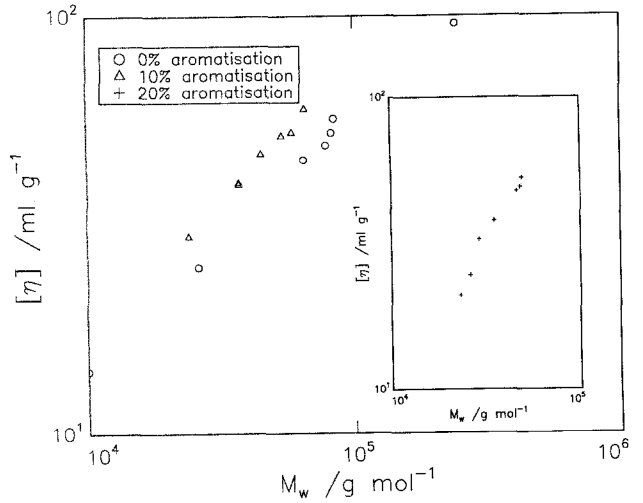


Figure 4 Mark–Houwink plots of intrinsic viscosity data for partially aromatized polymers in NMP at 298 K; inset shows data for 20% aromatization

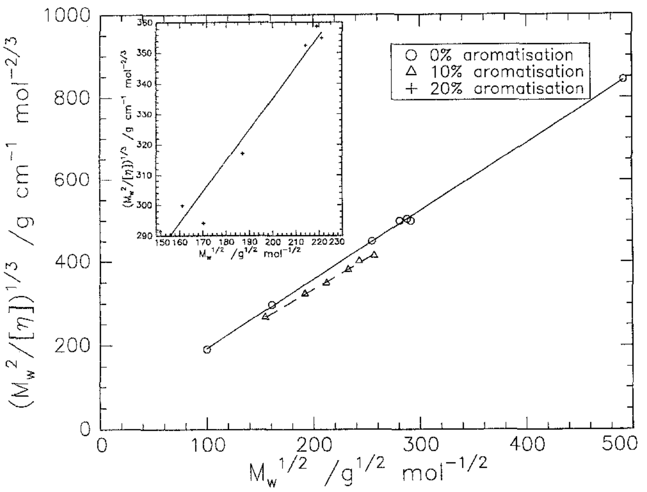


Figure 5 Intrinsic viscosity data plotted according to the Bohdanecký procedure (equation (14)); inset shows data for 20% aromatization

polymers were obtained for NMP solutions of polymers with 0, 10 and 20% aromatization. Mark–Houwink plots of these data are shown in *Figure 4* and from the linear least-squares fits to the data we obtain the following relationships:

$$0\%\ [\eta] = 0.054\,\bar{M}_{\mathrm{w}}^{0.61}$$

$$10\%\ [\eta] = 0.025\,\bar{M}_{\mathrm{w}}^{0.70}$$

$$20\%\ [\eta] = 2 \times 10^{-4}\,\bar{M}_{\mathrm{w}}^{1.15}$$

where all of these intrinsic viscosities are in units of ml g^{-1}.

DISCUSSION

The exponents in the Kuhn–Mark–Houwink relationships suggest that aromatization is accompanied by a partial change of configuration of the molecule to a more extended rod-like configuration. A parameter which can be used to quantify the extent of 'stiffening' is the persistence length, *a*. This parameter is used in the Yamakawa–Yoshizaki–Fuji theory[19,20] of the hydrodynamics of semiflexible or worm-like chains, along with the shift factor, M_L, and effective hydrodynamic diameter of the molecule in solution. We use this theory here, in the simplified form suggested by Bohdanecký[24], for interpretation of the intrinsic viscosity data. Our discussion below is restricted to percentage aromatizations between 0 and 20%, thus avoiding any complications due to bimodal molecular weight distributions.

The appropriate equation is as follows:

$$(\bar{M}_{\mathrm{w}}^2/[\eta])^{1/3} = A_\eta + B_\eta \bar{M}_{\mathrm{w}}^{1/2} \tag{14}$$

where

$$A_\eta = A_0 M_L \Phi_{0\infty}^{-1/3} \tag{15}$$

and

$$B_\eta = B_0 \Phi_{0\infty}^{-1/3} \left(\frac{M_L}{2a}\right)^{1/2} \tag{16}$$

In the above, $\Phi_{0\infty}$ is the universal viscosity constant, $B_0 = 1.05$ and A_0 is a function of the reduced diameter of the molecule d_r, where

$$d_r = d/2a \tag{17}$$

and the parameter d is the diameter of the molecules.

The relationship between d_r and A_0 depends on the value of d_r, e.g.

$$\log(d_r^2/A_0) = 0.173 + 2.158 \log d_r \quad (d_r \leqslant 0.1) \tag{18}$$

$$\log(d_r^2/A_0) = 0.795 + 2.78 \log d_r \quad (0.1 \leqslant d_r \leqslant 0.4) \tag{19}$$

Knowing the partial specific volume of the polymer, a value of d_r^2/A_0 can be calculated as follows:

$$d_r^2/A_0 = (4\Phi_{0\infty}/(1.215\pi N_A))(\bar{v}_2/A_\eta)B_\eta^4 \tag{20}$$

A value of d_r is then obtained using equations (18) or (19), and is subsequently used to evaluate A_0. This value is then combined with A_η to give M_L, which together with the value of B_η can be used to obtain a value for the persistence length. This procedure relies on having reliable values for A_η and B_η; *Figure 5* shows intrinsic viscosities plotted according to equation (14) and the linear least-squares fit to these data. Values of the shift factor, M_L, the persistence length, *a*, and the molecular diameter are given in *Table 2*. The relative changes in the value of the persistence length are consistent with the view that increased conversion of DHCDDMC units in the molecule to *p*-phenylene units leads to a straightening of the molecule and a more rod-like character being imparted. The absolute values of the persistence lengths and shift factors are in agreement with values recorded

Table 2 Shift factor, persistence length and molecular diameter obtained from Bohdanecký plots

Amount of aromatization (%)	M_L (Å)	a (Å)	d (Å)
0	12.5	11.8	20
10	43.8	27.4	8.5
20	88.4	128.9	12.9

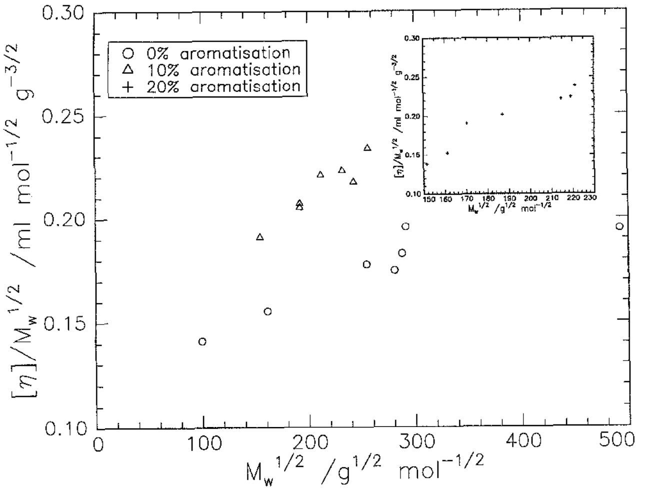


Figure 6 Stockmayer–Fixman plots for the intrinsic viscosity data for 0%, 10% and 20% aromatized polymer in NMP solution; inset shows data for the 20% aromatized polymer

Table 3 Data obtained from Stockmayer–Fixman plots

Amount of aromatization (%)	K_θ	$(\langle r^2\rangle_0/M)^{1/2}$ (10^{-9} cm)	B (10^{-27} cm^3)	χ
0	0.136	7.8	6.65	0.16
10	0.125	7.6	3.35	0.33

for other polymers. For the unconverted polymer the persistence length is of the same order of magnitude as conventional vinyl polymers. Polystyrene is reported to have $a = 19$ Å, while syndiotactic poly(methyl methacrylate) has a persistence length of ca. 30 Å. Similarly the shift factors obtained have values which are of the same order of magnitude as those reported for other polymers. Further discussion of these values is postponed until later.

The Kuhn–Mark–Houwink exponents for 0 and 10% aromatization suggest that any rigid-rod-like characteristics are not strong and consequently the extrapolation procedures developed in the application of two-parameter theories for continuous chain macromolecules may also be applicable. We apply only one here, namely the Stockmayer–Fixman extrapolation[22]:

$$\frac{[\eta]}{\bar{M}_{\mathrm{w}}^{1/2}} = K_\theta + 0.51\Phi_{0\infty} B\bar{M}_{\mathrm{w}}^{1/2} \qquad (21)$$

where

$$K_\theta = \Phi_{0\infty}(\langle r^2\rangle_0/M)^{3/2}$$

and

$$B = \left(\frac{\bar{v}_2^2}{V_1 N_{\mathrm{A}}}\right)(1-2\chi)$$

while V_1 is the molar volume of the solvent which has a Flory–Huggins interaction parameter of χ with the polymer. Stockmayer–Fixman plots for polymers with percentage aromatizations of 0, 10 and 20 are shown in *Figure 6*. For 0 and 10% aromatization linear plots are obtained through which reasonable least-squares lines can be drawn. Although this is also true for the 20% aromatized polymer, the intercept obtained is negative and this is physically unreal if the Stockmayer–Fixman procedure is applicable. For the 0 and 10% aromatizations, the values of K_θ, $(\langle r^2\rangle_0/M)^{1/2}$, B and χ that are obtained are set out in *Table 3*.

According to the theory of Yamakawa and Fujii[23] for one extreme of the worm-like chain model, i.e. the random flight Gaussian chain, then:

$$(\langle r^2\rangle_0/M)^{1/2} = (2a/M_L)^{1/2} \qquad (22)$$

Using the values obtained for a and M_L from the Bohdanecký plot (*Table 2*) we do not obtain exact agreement with the values of $(\langle r^2\rangle_0/M)^{1/2}$ in *Table 3*; values of ca. 11×10^{-9} cm are given from M_L and a for both 0 and 10% aromatization. However, these are sufficiently close to be acceptable. The values of $(\langle r^2\rangle_0/M)^{1/2}$ obtained from the Stockmayer–Fixman plots are of the same order of magnitude as those obtained for vinyl polymers and suggest that the chain is not particularly stiff up to a 10% aromatization, which is borne out by the values of a obtained from the Bohdanecký procedure. We have remarked above that a Stockmayer–Fixman analysis of the 20% aromatized sample produced a negative intercept. This is due to the restricted molecular weight range available for this polymer as a result of the degradation which accompanies aromatization. Even with a persistence length of ca. 130 Å, if the molecular weight were sufficiently high the molecule would behave as a Gaussian distribution of persistence lengths and for these high molecular weights the Stockmayer–Fixman procedure would be applicable. This view is confirmed by using the available viscosity data for the stiff chain polymer, poly(hexylisocyanate) in hexane solutions[24]. For molecular weights of this polymer less than 6×10^5, Stockmayer–Fixman analysis of these data produces a negative intercept. Similar analysis of higher-molecular-weight poly(hexylisocyanate) data results in a positive intercept from which the value of $(\langle r^2\rangle_0/M)^{1/2}$ obtained suggests that the polymer backbone is considerably larger than an equivalent freely rotating chain.

Light scattering values of $\langle s^2\rangle_{\mathrm{w}}$ can also be utilized to produce values of M_L and a. From the expression for the radius of gyration of a worm-like chain, Murakami and coworkers[24] obtained the approximation of equation (23) from equation (4), as follows:

$$(\bar{M}_{\mathrm{w}}/\langle s^2\rangle_{\mathrm{w}})^{1/2} = (3M_L/a)^{1/2}[1 + 3aM_L/2\bar{M}_{\mathrm{w}}] \qquad (23)$$

As long as $\bar{M}_{\mathrm{w}}/(4aM_L) > 1$, then equation (23) has less than 1% deviation from the exact expression for the radius of gyration. For the case in which the molecular weight of the polymer is sufficiently small that $\bar{M}_{\mathrm{w}}/(4aM_L) < 1$, Zhang *et al.*[25] have shown the following to apply:

$$(\bar{M}_{\mathrm{w}}^2/12\langle s^2\rangle_{\mathrm{w}})^{2/3} = M_L^{4/3} + (2/15)(M_L^{1/3}/a)\bar{M}_{\mathrm{w}} \qquad (24)$$

The range of molecular weights available here was such that equation (23) was applied to the data for the unaromatized and 10% aromatized polymers and equation (24) to the 20% aromatized material because of the restricted range of molecular weights available for this polymer. *Figure 7* shows the data plotted according to these two equations and the linear least-squares fits to the data. Although the data points are rather scattered, least-squares fits have been drawn through the points to

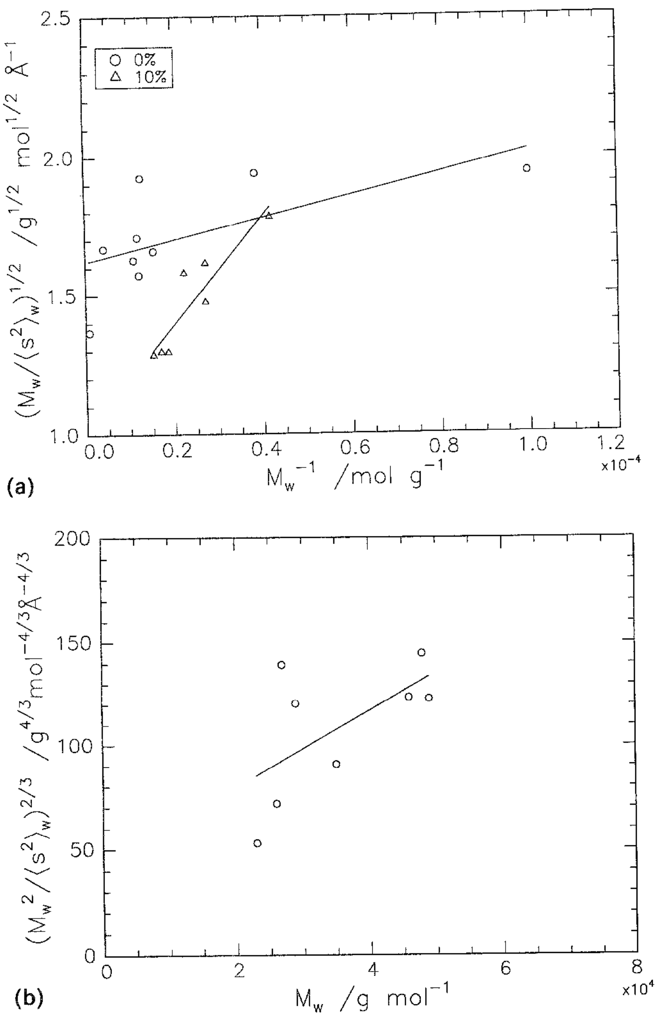


Figure 7 (a) Molecular weight and mean square radius of gyration plotted according to the equation of Murakami (equation (23)): (O) 0% aromatization; (Δ) 10% aromatization. (b) The same data for 20% aromatization plotted according to the equation of Zhang (equation (24))

Table 4 Persistence lengths and shift factors obtained from the mean square radius of gyration values from light scattering measurements

Amount of aromatization (%)	a (Å)	M_L (Å^{-1})
0	31	26
10	141	46
20	181	16.5

obtain M_L and a. Values of the persistence length and the shift factor that are obtained are given in *Table 4*. The persistence length shows the same behavioural trend as was observed in those values of a obtained from the viscometry data, i.e. an increase in a as the aromatization increased. However, the values are much larger than those obtained from the Bohdanecký analysis of viscosity data, particularly for the 10% aromatization where the light scattering value of a is almost ten times the value obtained from viscometry. Similarly, the shift factors obtained in this way differ from those given by the viscosity data and moreover there now appears to be no general trend in the values of M_L. The range of values of M_L may be due to the rather scattered nature of the data and the collapsing of the molecular weights of the partially aromatized polymers. What is particularly disturbing is the small value of M_L for the 20% aromatized polymer from the Zhang plot; we can only attribute this to the highly scattered data points. Furthermore, light scattering measurements sample different moments of the molecular-weight distribution from those sampled by viscosity measurements and for 20% aromatization $\bar{M}_w/\bar{M}_n$ values of ca. 2 are common. Thus the influence of this different sampling may be important. An additional factor we have ignored is that the partially aromatized polymers are 'blocky' *copolymers* and the aromatized units clearly have a very different refractive index to the unaromatized material (*Table 1*). This means that the molecular weight and radius of gyration that are obtained for the 10 and 20% aromatized polymers are *apparent* values. The extraction of true values of $\bar{M}_w$ requires light scattering measurements in three different solvents and the *SRII* of the 100% aromatized polymer. This latter parameter is experimentally inaccessible and furthermore a change of solvent will alter the radius of gyration values. Consequently, it is not surprising that the persistence lengths obtained by viscometry and light scattering differ in their absolute values.

Lastly we turn to the two topics of excluded volume effects and optical anisotropy. As the persistence length becomes larger then intermolecular excluded volume effects should become attenuated. Indeed, equations (3) and (4) are obtained by presuming the absence of excluded volume effects. Nonetheless, if the molecule is sufficiently long there will be excluded volume effects and there will be a critical contour length, L_c, associated with this change from unperturbed behaviour. The estimates of L_c[26,27] cover a wide range from ca. $2a$ to ca. $100a$ with the bulk of the experimental evidence supporting the latter. Since $L = \bar{M}_w/M_L$ we are able to calculate the values of L for the polymers used here. For the unaromatized polymer, the range of L explored is 34 860 to 286 Å using the M_L values from viscometry. If the upper estimate of L_C is used, then only the two highest-molecular-weight specimens should show any evidence of excluded volume behaviour. However, the exponent in the Mark–Houwink relationship and the excellent agreement of the data to a Stockmayer–Fixman relationship for this polymer suggest that L_c should be considerably smaller than $100a$. For the 10% aromatized polymer the range of L is 270 to 100 Å and no sample should have any excluded volume behaviour by whatever criterion defines L_C. The 20% aromatized polymer has $70 \leqslant L \leqslant 150$(Å) and again all specimens should have an unperturbed configuration.

Finally, although there is clear evidence for an increase in the stiffness of the molecules as aromatization proceeds we note that optical anisotropy was not observed in the scattered light from solutions of any of the polymers. Consequently up to 20% aromatization, although the molecule becomes increasingly stiff, the polarizability tensors of the molecule are still arranged isotropically and thus the molecules are far from being truly rigid rods.

CONCLUSIONS

Using dilute solution viscometry and classical intensity light scattering on N-methylpyrrolidinone solutions of partially aromatized precursor polymers of poly(*p*-phenylene), we have shown that the persistence length increases as aromatization increases. Both techniques show this trend. Values from intrinsic viscosity measurements for the persistence length range from ca. 12 to 130 Å as the extent of aromatization increases from 0 to 20%. Values from light scattering, although showing the same trend, are larger and there are additional factors which suggest that the values determined from viscosity may be more reliable. The changes in persistence length are commensurate with a stiffening of the molecule as the number of phenylene units in the backbone increases. This process can only be followed up to an aromatization of ca. 20%; for high aromatizations earlier work showed that aggregation becomes an increasingly important facet in the structure of the partially aromatized species.

ACKNOWLEDGEMENTS

JRH thanks the Science and Engineering Research Council for the provision of a maintenance grant as part of a CASE award with ICI Chemicals and Polymers Ltd.

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