Characterization of chain dimensions of poly(ε-caprolactone) diols in THF by size-exclusion chromatography coupled with multi-angle light scattering (SEC-MALS)

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Abstract In this work, we studied the chain dimensions, shape, and thermodynamic characteristics of poly(ε-caprolactone) diols (HO-PCL-OH) in solution. PCL diol samples of different molecular weights and architectures were synthesized using immobilized *Yarrowia lipolytica* lipase as catalyst. Gel permeation chromatography (GPC) with online right-angle laser-light scattering (RALLS), differential viscometer (DV), and interferometric refractometer IRS detectors offered a proper way to obtain information on thermodynamic characteristics and chain flexibility. The weight-average molecular weights of the PCL diol samples (M_w) ranged from 2,750 to 13,120 uma. The *z*-average radius of hydrodynamic volume ($<R_h^2>_z^{1/2}$) vs. *z*-average molecular weight curve (M_z) could be satisfactorily fitted to a power-law equation. Mark–Houwink–Sakurada parameters ($K = 2.74 \times 10^{-3}$ dL/g and $a = 0.64$) were derived from the plots of $[\eta]_w$ against M_w. The overall results clearly suggest that a flexible geometry is present in tetrahydrofuran (THF) solution of PCL at 33 °C. Unlike other PCL systems, PCL diols are more hydrophilic and expected to form associated species. They behave differently from common hydrophobic polymers and do not strictly conform to thermodynamic relationships generally used in Polymer Science. A more compact geometry is present for M_n lower than 4,000 Da. For higher molecular weights, the chain expands and become more elongated. Plots of *ln* $[\eta]_w$ against *ln* M_w (MHS equation) and of *log* R_{hz} against *log* M_z suggest that PCL diols behave as flexible chains in a good solvent.

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Introduction

Poli(ε-caprolactone)(PCL) is a biodegradable and biocompatible polymer widely used in surgical implants, packaging materials, pharmaceutical formulations, polymer blends, and in applications ranging from controlled-release drug delivery systems to tissue engineering [1–4].

Telechelic poly(ε-caprolactone) diols (HO-PCL-OH) are generally prepared using ring-opening polymerization of ε-caprolactone initiated by diols. They are widely used as precursors of many polymer derivatives, including poly(ester-urethanes), block copolymers, and other advanced architectures [4–6].

Some reports have appeared in the literature on the physicochemical characterization of diluted PCL solutions [7–11]. PCL has been studied using a number of techniques such as light scattering (LS), osmometry, and viscometry on various solvents at different temperatures [8, 9]. Data reported by these authors include characteristic ratio values C_∞ in the range of 4.3 to 5.9. Theoretical calculations, on the other hand, have predicted a value of $C_\infty = 6$ for PCL[10]. Mays et al. reported

viscometric radius values (1.97 to 5.69 nm) and a characteristic ratio of 5.0 using tetrahydrofuran (THF) as solvent [11].

In the present paper, we report on a series of 43 samples of PCL diols (see Table 1) that were prepared using *Yarrowia lipolytica* lipase biocatalysis in the presence of different

initiators [12], and characterized using gel permeation chromatography with multi-angle light scattering (GPC-MALS). Although some studies have been reported on the solution behavior of PCL, they have all used commercial samples with conventional macromolecular architecture, with low to

Table 1 Samples used in this study

Sample	Enzyme	Glycol	M_w	M_w / M_n
PCL1	YLL-1026	PEG200, 1 mmol	6060	1.04
PCL2	YLL-1026	PEG400, 1 mmol	3428	1.26
PCL3	YLL-1026	PEG1000, 0.1 mmol	8386	1.1
PCL4	YLL-1026	PEG350 1 mmol	2842	1.23
PCL5	YLL-K2629	PEG200, 1 mmol	2747	1.05
PCL6	YLL-K2629	PEG400, 1 mmol	12450	1.03
PCL7	YLL-K2629	PEG350, 1 mmol	4370	1.30
PCL8	YLL-amb15	PEG200, 1 mmol	5116	1.31
PCL9	YLL-amb15	PEG400, 1 mmol	4844	1.15
PCL10	YLL-amb15	PEG350, 1 mmol	6700	1.7
PCL11	YLL-1026	DEG, 1 mmol	4633	1.08
PCL12	YLL-1026	DEG, 0.5 mmol	13120	1.03
PCL13	YLL-1026	DEG, 0.25 mmol	9313	1.17
PCL14	YLL-K2629	DEG, 0.5 mmol	5130	1.42
PCL15	YLL-amb15	DEG, 1 mmol	3255	1.31
PCL16	YLL-1026	EG, 0.5 mmol	6736	1.11
PCL17	YLL-1026	EG, 0.25 mmol	7528	1.16
PCL18	YLL-K2629	EG, 1 mmol	3312	1.22
PCL19	YLL-amb15	EG, 1 mmol	530	1.32
PCL20	YLL-1026	TEG, 0.5 mmol	5670	1.13
PCL21	YLL-1026	TEG, 0.25 mmol	5484	1.36
PCL22	YLL-amb15	TEG, 1.5 mmol	3528	1.25
PCL23	YLL-amb15	TEG, 1 mmol	5620	1.40
PCL24	YLL-1026	1,3PROP, 0.5 mmol	6260	1.14
PCL25	YLL-1026	1,3PROP, 0.25 mmol	6728	1.14
PCL26	YLL-K2629	1,3PROP, 1.0 mmol	4684	1.24
PCL27	YLL-K2629	1,3PROP, 0.5 mmol	10070	2.00
PCL28	YLL-1026	1,4 BUT, 2.0 mmol	3420	1.16
PCL29	YLL-1026	1,4 BUT, 0.5 mmol	5872	1.19
PCL30	YLL-1026	TETRA, 2.0 mmol	3890	1.19
PCL31	YLL-1026	TETRA, 1.0 mmol	3970	1.22
PCL32	YLL-K2629	TETRA, 1.0 mmol	2846	1.33
PCL33	YLL-amb15	TETRA, 1.5 mmol	4148	1.20
PCL34	YLL-amb15	TETRA, 1.0 mmol	3751	1.24
PCL35	YLL-1026	1,3 BUT, 2.0 mmol	4177	1.20
PCL36	YLL-K2629	1,3 BUT, 2.0 mmol	3430	1.33
PCL37	YLL-amb15	1,3 BUT, 4.0 mmol	3577	1.30
PCL38	YLL-1026	1,6 HEX, 0.1 mmol	11080	1.21
PCL39	YLL-1026	1,6 HEX, 0.5 mmol	10180	1.06
PCL40	YLL-1026	1,8 OCT, 0.1 mmol	12300	1.16
PCL41	YLL-1026	1,8 OCT, 0.25 mmol	8092	1.32
PCL42	YLL-1026	NEOPENT, 0.1 mmol	11690	1.21
PCL43	YLL-1026	NEOPENT, 0.25 mmol	8111	1.12

PEG poly(ethylene)glycol, *DEG* diethylene glycol, *TEG* triethylene glycol, *EG* ethylene glycol, *1,3 prop* 1,3 propanediol, *1,4 BUT* 1,4 butanediol, *1,3 but* 1,3 butanediol, *TETRA* tetraethylene glycol, *1,6 HEX* 1,6 hexanediol, *1,8 OCT* 1,8 octanediol, *NEOPENT* neopentyl glycol, *R*=10 mmol caprolactone/ x mmol diol/ 12 mg lipase

medium molecular weights. The samples analyzed here are a unique set, as they were obtained by biocatalysis using a non-commercial lipase using a procedure developed in our laboratory. Solution behavior of these samples at 33 °C was analyzed using data obtained by size-exclusion chromatography with an online right-angle laser-light scattering (RALLS) photometer, differential viscometer (DV), and interferometric refractometer detector (IRS). Weight-average molecular weights of the prepared samples ranged from 2,750 to 13,120 uma. The hydrodynamic radii ($<R_h^2>^{1/2}$ of these samples were found to correlate well with the hard core radii $<r>^{1/2}$ expected from PCL diol molecular weights. For lower molecular weights (Mn <4,000 Da), polymer chains adopt a more compact conformation in THF. At higher molecular weights, larger deviations from a spherical geometry occur.

Theoretical considerations

Thermodynamic behavior of dilute polyester solutions

The behavior of polylactone derivatives (aliphatic polyesters) in dilute solutions is markedly different from that of stiff-chain polymers. The tendency of these polymers is to form flexible chains in common solvent systems. This is mainly due to the high flexibility of polyester chains that possess several methylene groups. Chain flexibility increases with the degree of rotation along the chain carbon–carbon bonds, which leads to a decrease in chain dimensions in solution. Smaller dimensions are observed in theta solvents compared to good solvents [8, 9, 13].

End-to-end distance, $<r^2>^{1/2}$, and the radius of gyration $<R_g^2>^{1/2}$ are useful parameters for characterizing the conformational characteristics of polymer chains [13, 14], as they are measures of the polymer size averaged over all available polymer conformations. Another important parameter is the hydrodynamic radius $<R_h^2>^{1/2}$, which corresponds to the volume of a hydrodynamically equivalent sphere. These parameters, in turn, are dependent upon polymer molecular weight. Long- and short-range steric interactions between neighboring or near-neighboring polymer segments are directly related to macromolecular size. Molecular interactions depend upon solvent and temperature.

The hydrodynamic radius $<R_h>$ of a polymer chain can be determined by molecular weight using a power-law equation

$$\langle R_h^2 \rangle^{1/2} = K' M^{\nu} \tag{1}$$

where parameter ν is characteristic of polymer chain flexibility. Values of ν have been calculated theoretically for various

macromolecular shapes. A value of 0.33 has been recorded for hard spheres, 0.5 for polymers under theta conditions, and 1 for rigid rods [15].

Another important experimentally measured parameter is the intrinsic viscosity [η]. Intrinsic viscosity measured at θ temperature or in poor solvents, $[\eta]_\theta$, is proportional to the ratio of effective hydrodynamic volume of the polymer to its molecular weight M [13].

$$[\eta]\theta \sim \frac{\langle r^2 \rangle^{3/2}}{M} \tag{2}$$

Under perturbed conditions, this equation takes the form

$$[\eta] = \Phi \frac{\langle r^2 \rangle^{3/2}}{M} = \Phi \left(\frac{\langle r_o^2 \rangle}{M} \right)^{3/2} M^{1/2} \alpha^3 \tag{3}$$

where $\Phi \approx 2 \times 10^{21}$ dl/g mol cm^3 is the universal constant, $<r_o^2>^{1/2}$ and $<r^2>^{1/2}$ are the mean root square of the end-to-end distance for unperturbed and perturbed chains, respectively, M is the molecular weight and α the chain expansion coefficient.

Equations 2 and 3 can be correlated with the Mark–Houwink–Sakurada (MHS) equation, which describes the relationship between intrinsic viscosity and molecular weight

$$[\eta] = K M^a \tag{4}$$

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Constants K and a vary with polymers and solvents. Under θ conditions (compact chains) a=0.5; higher values of a are associated with more flexible chains.

Experimental procedure

Samples and materials

ε-CL (Sigma-Aldrich Corp.) was dried over calcium hydride and distilled under reduced pressure before use. Polyethylene glycol (PEG200, PEG400, and PEG1000), diethylene glycol (DEG), ethylene glycol (EG), triethylene glycol (TEG), tetraethylene glycol (TETR), 1,3- propanediol (1,3 prop), 1,3 and 1,4-butanediol (1,3 and 1,4-but), 1,6 hexanediol (1,6 hexa), 1,8-octanediol (1,8 oct), and neopentyl glycol (NEOPENT) were obtained from Sigma-Aldrich and used as received. Lewatit VP OC 1206, Lewatit VP OC K2629, and Amberlyst 15 were obtained from Sigma-Aldrich. *Yarrowia*

lipolytica lipase (YLL) was obtained according to the procedure described in the literature [12]. Polyester samples in this study were prepared by ring-opening polymerization of ε-caprolactone in the presence of diols, using biocatalysis by *Yarrowia lipolytica* lipase (YYL) [6] (see Table 1). YYL supported in different matrices was used. PCL1 to PCL9 samples were prepared from ε-caprolactone using polyethylene glycol (PEG) as initiator, whereas PCL11 to PCL45 were obtained from PCL and various diols: ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TETR), 1,3- propanediol (1,3 prop), 1,3 and 1,4-butanediol (1,3 and 1,4-but), 1,6 hexanediol (1,6 hexa), 1,8-octanediol (1, 8 oct) and neopentyl glycol (NEOPENT).

Samples **PCL1** (10 mmol ε-CL/ 1 mmol PEG200/12 mg YLL-1026), **PCL2** (10 mmol ε-CL/ 1 mmol PEG400/12 mg YLL-1026), **PCL3** (10 mmol ε-CL/ 0.1 mmol PEG1000/ 12 mg YLL-1026), **PCL4** (10 mmol ε-CL/ 1 mmol PEG350/12 mg YLL-1026), **PCL5** (10 mmol ε-CL/ 1 mmol PEG200/12 mg YLL-K2629), **PCL6** (10 mmol ε-CL/ 1 mmol PEG400/12 mg YLL-K2629), **PCL7** (10 mmol ε-CL/ 1 mmol PEG350/12 mg YLL-K2629), **PCL8** (10 mmol ε-CL/ 1 mmol PEG200/12 mg YLL-Amberlyst15), **PCL9** (10 mmol ε-CL/ 1 mmol PEG400/12 mg YLL-Amberlyst15), **PCL10** (10 mmol ε-CL/ 1 mmol PEG350/12 mg YLL-Amberlyst15), **PCL11** (10 mmol ε-CL/ 1 mmol DEG/12 mg YLL-1026), **PCL12** (10 mmol ε-CL/ 0.5 mmol DEG/12 mg YLL-1026), **PCL13** (10 mmol ε-CL/ 0.25 mmol DEG/12 mg YLL-1026), **PCL14** (10 mmol ε-CL/ 0.5 mmol DEG/12 mg YLL-K2629), **PCL15** (10 mmol ε-CL/ 1 mmol DEG /12 mg YLL-Amberlyst15), **PCL16** (10 mmol ε-CL/ 0.5 mmol EG/12 mg YLL-1026), **PCL17** (10 mmol ε-CL/ 0.25 mmol EG/12 mg YLL-1026), **PCL18** (10 mmol of ε-CL/ 1.0 mmol of EG/ 12 mg YLL-K2629), **PCL19** (10 mmol of ε-CL/ 1.0 mmol of EG/ 12 mg YLL-Amberlyst15), **PCL20** (10 mmol ε-CL/ 0.5 mmol TEG /12 mg YLL-1026), **PCL21** (10 mmol ε-CL/ 0.25 mmol TEG/12 mg YLL-1026), **PCL22** (10 mmol ε-CL/ 1.5 mmol TEG /12 mg YLL-Amberlyst15), **PCL23** (10 mmol ε-CL/ 1 mmol TEG /12 mg YLL-Amberlyst15), **PCL24** (10 mmol ε-CL/ 0.5 mmol 1,3-prop /12 mg YLL-1026), **PCL25** (10 mmol ε-CL/ 0.25 mmol 1,3-prop /12 mg YLL-1026), **PCL26** (10 mmol ε-CL/ 1 mmol 1,3-prop /12 mg YLL-K2629), **PCL27** (10 mmol ε-CL/ 0.5 mmol 1,3-prop / 12 mg YLL-K2629), **PCL28** (10 mmol ε-CL/ 2 mmol 1,4-but /12 mg YLL-1026), **PCL29** (10 mmol ε-CL/ 0.5 mmol 1,4-but /12 mg YLL-1026), **PCL30** (10 mmol ε-CL/ 2 mmol Tetra /12 mg YLL-1026), **PCL31** (10 mmol ε-CL/ 1 mmol Tetra / 12 mg YLL-1026), **PCL32** (10 mmol ε-CL/ 1 mmol Tetra / 12 mg YLL-K2629), **PCL33** (10 mmol ε-CL/ 1.5 mmol Tetra /12 mg YLL-Amberlyst15), **PCL34** (10 mmol ε-CL/ 1 mmol Tetra /12 mg YLL-Amberlyst15), **PCL35** (10 mmol ε-CL/ 2 mmol 1,3-but /12 mg YLL-1026), **PCL36** (10 mmol ε-CL/ 2 mmol 1,3-but /12 mg YLL-K2629), **PCL37** (10 mmol ε-CL/ 2 mmol 1,3-but /12 mg YLL-Amberlyst15), **PCL38**

(10 mmol ε-CL/ 0.1 mmol 1,6-hexa /12 mg YLL-1026), **PCL39** (10 mmol ε-CL/ 0.5 mmol 1,6-hexa /12 mg YLL-1026), **PCL40** (10 mmol ε-CL/ 0.1 mmol 1,8-octa /12 mg YLL-1026), **PCL41** (10 mmol ε-CL/ 0.25 mmol 1,8-octa / 12 mg YLL-1026), **PCL42** (10 mmol ε-CL/ 0.1 mmol NEOPENT /12 mg YLL-1026), and **PCL43** (10 mmol ε-CL/ 0.25 mmol NEOPENT /12 mg YLL-1026) were separately placed in 10 mL vials previously dried. Vials were stoppered with a Teflon silicon septum and placed in a heated bath at 120 °C for 24 h. No inert atmosphere was used. After the reaction was complete, the enzyme was filtered off. PCL diols were dried at 70 °C under a vacuum for 12 h, and stored at ambient temperature in a vacuum desiccator until used.

Characterization

The characterization of PCL diols was performed using size-exclusion chromatography (SEC) equipped with a refractive index detector, viscometer, and right-angle laser-light scattering detector (RALLS). The chromatographic set-up used consists of an Alliance HPLC Waters 2695 Separation Module having a vacuum degassing facility on online, an autosampler, a quaternary pump, a column thermostat, and a Waters 2414 Differential Refractometer for determining the distribution of molecular weight.

A bank of four columns with the following characteristics was used : HSPgel: HR 1.0, HR 2.5, HR 4.0, and HR MB-M (dimensions 150 mm×6.0 mm) with pore sizes of 50 Å, 500 Å, $1.0×10^4$ and a mixed bed pore size (100 Å to $1.0×10^6$ Å) respectively, and particle size 3 and 5 μm. The temperature of the columns was controlled at 33 °C by the thermostat.

The SEC was used online with the following multi-detector system supplied by Wyatt Technology Corporation (Santa Barbara, CA, USA): a multi-angle light-scattering (MALS) Dawn EOS photometer that measures the intensity of the scattered light at 16 angular locations ranging from 12.5° to 164.9°; a ViscoStar viscometer for measuring the differential pressure in a four-capillary bridge; and an interferometer refractometer detector (Optilab rEX) as a concentration detector. Molecular weight distribution was obtained using Alliance Empower software. However, to obtain the absolute values for molar masses, radius of gyration, and intrinsic viscosity distribution data, the Wyatt ASTRA V® for Windows (version 5.3.2.10, Wyatt Technology Corp.) software was used.

HPLC-grade tetrahydrofuran (THF), previously filtered (in a 0.45 μm pore size filter) and degassed, was used as the eluent. For sample preparation, 50 mg of PCL diol was dissolved in THF at 35 °C. The warm solution was filtered through 0.2 μm cellulose acetate membrane filters.

Typical conditions were as follows: flow rate of 0.5 ml/min; 100 μL injection volume; analysis time per sample, 35 min.

For cross-checking, the columns were calibrated using 18 polystyrene (PS) standards in a range of molecular mass 486 to 4.11E+6 g/mol and PDI in a range of 1.24–1.03 (Polymer Standards Service-USA, Inc.). At least two injections of each standard were run for fitting the calibration curve. The calibration curve was adjusted to a third-order polynomial with 36 data points.
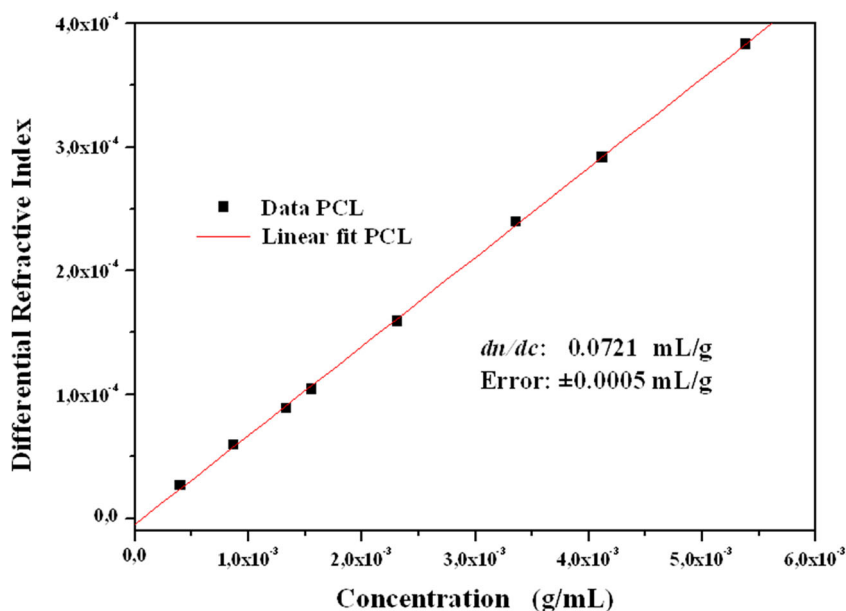
The concentration of the PS standards dissolved in THF varied between 0.1 and 2.0 mg/mL, depending upon the molecular weight. The PCL samples were also dissolved in THF at a concentration of around 2.0 mg/mL. All solutions were filtered and degassed online prior to analysis.

Measurements

The evaluation of radius of gyration $<r_g>$, hydrodynamic radius $<r_h>$, and intrinsic viscosity $[\eta]$ moments data was carried out with a ViscoStar detector equipped with a four-capillary bridge to measure the differential pressure. The dimensions of the capillary tube are *0.010 in* internal diameter and *26 in* length. The maximum volume of each capillary tube is 80 μL.

The refractive index increment (dn/dc) value was measured using the Optilab rEX calibrated differential refractive index (DRI) detector. The equipment used a wavelength of 690 nm. Eight different concentrations of PCL solution ranging from 0.1 to 1.0 mg/mL were prepared and injected at 35 °C. The obtained dn/dc value was 0.0721 mL/g. The precision error on this value, as calculated from the DRI detector response, was approximately ±0.0005 mL/g (Fig. 1). Precision error, reported as percentage of relative standard deviation (%RSD) 2σ on both the M_w and $[\eta]$, was typically between 1.0 and 1.5 %. A value of 0.079 mL/g for the specific refractive index dn/dc for PCL has been reported in the literature [8].

The MALS photometer used a gallium arsenide (GaAs) laser operating at a nominal wavelength of 690 nm. The calibration constant was calculated using HPLC-grade toluene as standard, assuming a Rayleigh factor of 9.78×10^{-5} cm^{-1}. Three independent measurements (injections) were performed for the calibration. The obtained calibration constant was 8.457×10^{-6} Vcm^{-1}.

Normalization of the photodiodes was performed by measuring the scattering intensity of polystyrene standards (3.0×10^4 and 2.0×10^5 g/mol) dissolved in HPLC-grade THF, assuming isotropic scattering. The concentration of the polymer dissolved in THF was 2.0 mg/mL. The obtained value of dn/dc was 185 mL/g.

The exact concentrations of the polymer solutions were carefully determined in order to calculate the molecular parameters. The response area of each detector, combined with known values for Mw, PDI, R_g, $[\eta]$, and concentration, were used to obtain the instrument calibration constants for each detector. These constants were used for the conversion of each detector response into values for Mw, PDI, R_g, R_h, $[\eta]$, and dn/dc. Because the detector response attributed to the polymer was found at identical retention times and constant flow rate, the integration and baseline limits were kept invariant by the software, thus removing analysis subjectivity for these selections.

Results

SEC-MALS chromatography results

RI chromatograms (detection signal against elution times) for four samples (6, 11, 27, and 38 in Table 1) dissolved in THF

Fig. 1 Refractive index (*n*) versus concentration (*c*) increment of polymer solutions (PCL). The slope is the *dn/dc*

are depicted in Fig. 2. All three chromatograms appear to show a unimodal distribution. Data were processed as indicated in the section "Experimental procedure" by means of ASTRA V software, and the calculated molecular weights are shown in Table 1. The corresponding weight-average molecular weight for these samples, respectively, are 12.4, 4.6, 10.0 and 11 kg/mol. The weight-average molecular weights for PCL diol samples (M_w) ranged from 2,750 to 13,120 uma. Table 1 summarizes the weight-average molecular weights derived for the different samples. Other parameters obtained include hydrodynamic radii $R_h(w)$, intrinsic viscosities [η] and root mean square (rms) radii of gyration R_g.

Samples obtained in this work show low to moderate molecular weights, with narrow (PDI close to 1) to broad (PDI= 2) molecular weight distribution It is well known that the accuracy of molar mass measurement by SEC with LS is limited to M_w values in the range of 10^4 to 10^7 [16, 17], so most of the samples studied in this work were located in the lower limit of this technique.

Calculation of physicochemical parameters

The use of GPC with online RALLS, DV, and IRS techniques provides a reliable and easy method for obtaining information regarding thermodynamic characteristics, molecular conformation, and chain flexibility. The interrelation between intrinsic viscosity and molecular weight, as well as radius of gyration and molecular weight, can be determined. The combination of these techniques provides a separation of molecules based on their hydrodynamic size, along with a characterization of their molecular structure based on light-scattering measurements [16, 17].

In solvent solutions—such as THF—at room temperature, PCL behaves as a flexible chain and shows a random coil
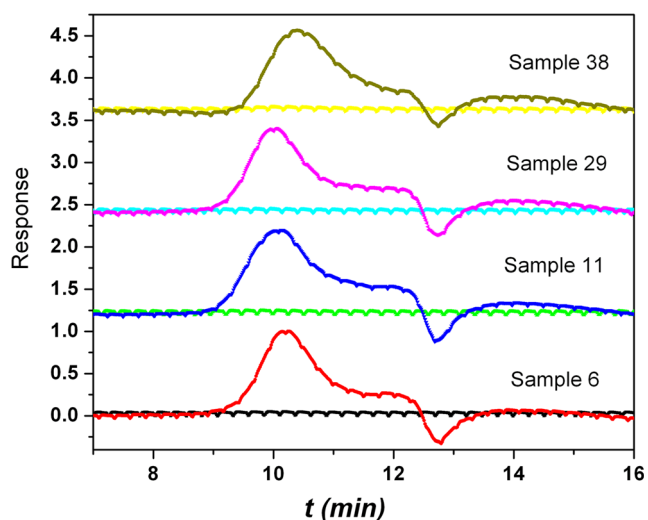
conformation [7–11]. For random coil polymers, the molecular volume V_i occupied in a solvent can be approximated to an equivalent sphere with a radius $\langle r \rangle^{1/2}$ [13, 14]. Polymer volume V_i can be derived from the $\langle r \rangle^{1/2}$, which is dependent upon the bulk density and molecular weight of PCL

$$\langle r^2 \rangle^{1/2} = \left[\left(\frac{3}{4\pi} \right) \frac{8M \times 10^{24}}{\rho No} \right]^{1/3} \qquad (5)$$

Assuming that bulk density for PCL is 1.15 g/mol [18], this equation gives the following dependence for $\langle r \rangle^{1/2}$ on molecular weight:

$$\langle r^2 \rangle^{1/2} = (2.75 \, M)^{1/3} \qquad (6)$$

Based on the number-average molecular weight reported in GPC-MALLS data, the sphere radius $\langle r^2 \rangle^{1/2}$ for the polymer was derived. Values of hydrodynamic radii $R_h(n)$ were derived from GPC-MALLS chromatograms as describes earlier.

Hydrodynamic radii $R_h(n)$ recorded by GPC-MALLS are directly proportional to the sphere radii $\langle r^2 \rangle^{1/2}$, as shown in Fig. 3 (correlation coefficient $R^2 = 0.92$). Average value for $R_h(n) / \langle r^2 \rangle^{1/2}$ is 1.45. However, data dispersion is observed. One important feature is that for number-average molecular weights M_n lower than 4,000 Da (which correspond to $R_h(n)$ values of around 22.5 Å), data points show lower dispersion (average $R_h(n) / \langle r^2 \rangle^{1/2}$ is 1.36 for these samples), which indicates that for these samples, the macromolecular shape more closely resembles a hard core sphere. PCLs with low molecular weights show a more compact configuration. For
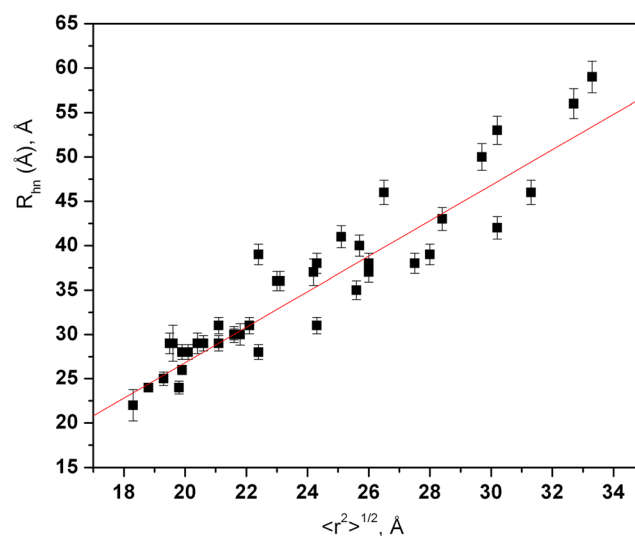

Fig. 2 RI chromatograms (differential refractive index n against time in minutes) for three polymer solutions (PCL). Differential pressure of each solution (baseline) is also shown

Fig. 3 Plot of first-moment hydrodynamic radius $R_h(n)$ against sphere radii $\langle r \rangle^{1/2}$ for samples listed in Table 1
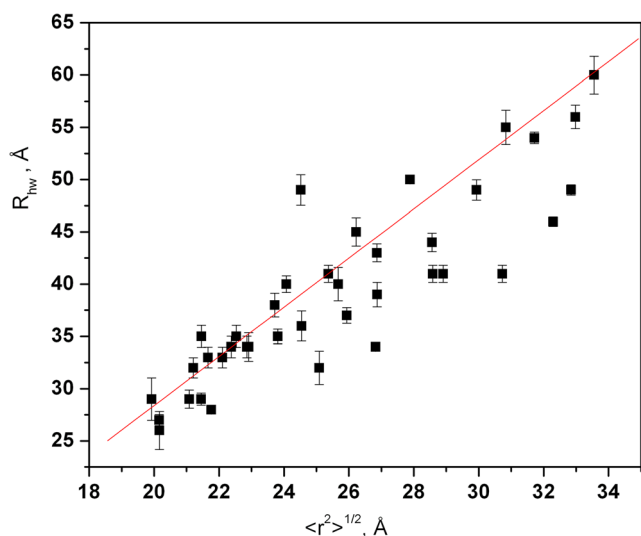
Fig. 4 Plot of second-moment hydrodynamic radius $R_w(n)$ against sphere radii $<r>^{1/2}$ for some of the samples listed in Table 1

Fig. 6 Plot of $\ln R_{hz}$ against $\ln M_z$ for some of the samples listed iin Table 1

higher molecular weights, $R_h(n) / <r^2>^{1/2}$ gradually increases to 1.77, indicating that as molecular weight increases, chain flexibility decreases, with larger molecular size and more elongated geometry.

A similar trend was observed for the plot of the second-moment hydrodynamic radii $R_h(w)$ as a function of sphere radii $<r^2>^{1/2}$ (see Fig. 4). Data dispersion is higher.

Data dispersion observed in Figs. 2, 3, 4, 5, 6, and 7 is mainly due to the conformation flexibility of the PCL derivatives studied and the limitations of the technique used . Data dispersion increases at higher molecular weights.

A plot of $\ln [\eta]_w$ against $\ln M_w$ is depicted in Fig. 5. From this plot, the parameters of the MHS equation were derived ($K=2.74\times10^{-3}$ and $a=0.64$): Thus, the MHS equation for PCL in THF is
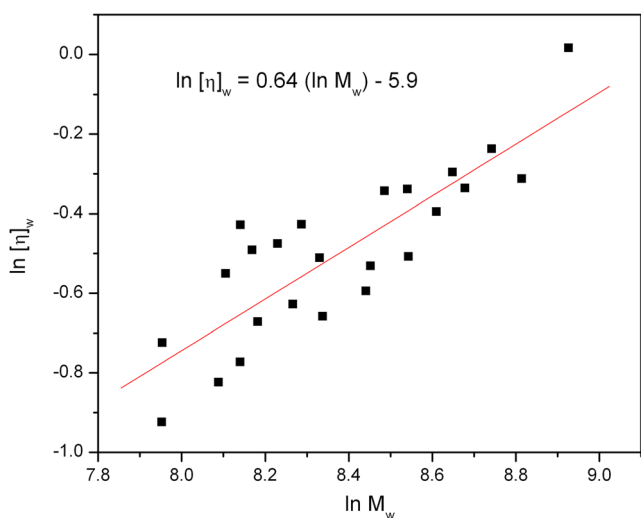
$$[\eta]_w = 2.74 \times 10^{-3} M_w^{0.64}$$
$$(2747 < M_w < 13120, \text{ correlation coefficient} = 0.85)$$

As previously mentioned, the value of MHS exponent (0.64) provides a measure of chain rigidity. For flexible chains in θ solvent, a value of 0.5 is observed, whereas for good solvents, a value in the range of 0.7 to 0.8 is expected. The recorded value indicates that THF tends to be a good solvent for PCL.

Information relevant to chain conformation can also be derived by plotting the logarithm of the z-average hydrodynamic radii (R_{hz}) against the logarithm of the z-average molecular weight. The exponent ν and constant K values were

Fig. 5 Plot of $\ln [\eta_w]$ against $\ln M_w$ for some of the samples listed in Table 1

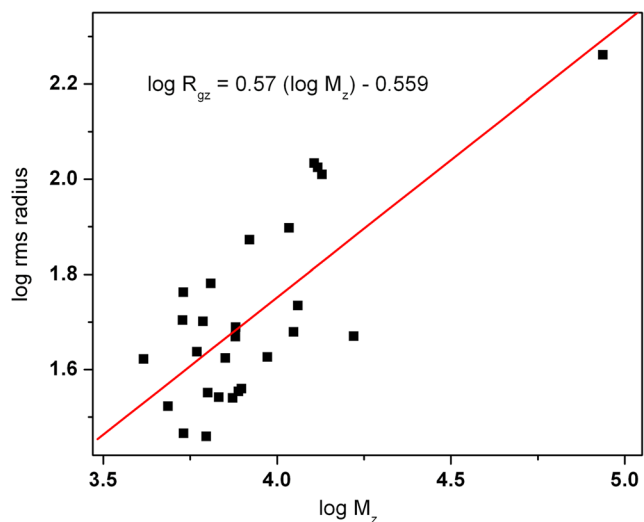**Fig. 7** Plot of $\log R_{gz}$ against $\log M_z$ for some of the samples listed in Table 1

derived from the plot, and the relationship obtained is represented by the following equation (in THF at 33 ° C):

$$R_{hz} = 5.2 \times 10^{-2} M_z^{0.51}$$
$$(2874 < M_z < 16600, \text{ correlation coefficient} = 0.745).$$

The recorded slope value (0.51) is in a range of 0.5 to 0.6, which corresponds to a random coil in a good solvent with borderline behavior. Recorded values for PCL in THF at 33 °C are in agreement with that reported by Mays et al. [11].

Information regarding molecular size can also be derived from the z-average root mean square (rms) radius of gyration versus molecular weight, which is obtained from the angular dependence of scattered light. The logarithm of z-average **rms** radii (R_{gz}) are depicted versus the logarithm of -z-average molecular weight (Fig. 7), giving the following equation (in THF at 33 ° C):

$$R_{gz} = 2.76 \times 10^{-1} M_z^{0.57}$$
$$(30 \text{ nm} < R_{gz} < 180 \text{ nm and } 4120$$
$$< M_z < 16600, \text{ correlation coefficient} = 0.75)$$

Values of $R_{gz} < 30$ nm were ignored because of measurement uncertainty.

Conclusions

Unlike other PCL systems, PCL diols are more hydrophilic and expected to form associated species. They behave differently from common hydrophobic polymers and do not strictly conform to thermodynamic relationships generally used in polymer science. In this work, we reported the application of a GPC/RALLS/DV/IRS multi-detector system to characterize molecular weights and shapes of PCL diols in THF at 33 °C. There has been controversy in the literature regarding the molecular shape of these substances, and on the actual dependence of molecular size with their molecular weight. It is commonly assumed that they are random coils with relative compact geometry, and that they behave similar to polyolefins. The overall results clearly suggest that a flexible geometry is present in THF solution of PCL at 33 °C. A more compact geometry is present for M_n lower than 4,000 Da. For higher molecular weights, the chain expands and becomes more elongated. Plots of *ln [η]$_w$* against *ln M$_w$* (MHS equation) and of *log R$_{hz}$* against *log M$_z$* suggest that PCL diols behave as flexible chains in a good solvent.

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