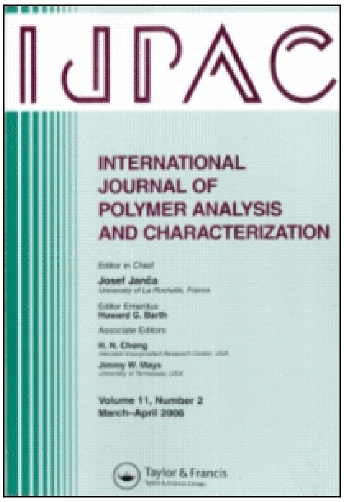

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Characterization of Poly(ε-Caprolactone) via Size Exclusion Chromatography with Online Right-Angle Laser-Light Scattering and Viscometric Detectors

Yi Huang[a]; Zhongde Xu[a]; Yiping Huang[b]; Dezhu Ma[b]; Jinchuan Yang[c]; Jimmy W. Mays[c]
[a] Department of Polymer Science and Engineering, East China University of Science and Technology, Shanghai, China [b] Department of Polymer Science and Engineering, China University of Science and Technology, Hefei, China [c] Department of Chemistry, University of Alabama, Birmingham, Alabama, USA

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Yi Huang and Zhongde Xu
Department of Polymer Science and Engineering,
East China University of Science and Technology,
Shanghai, China

Yiping Huang and Dezhu Ma
Department of Polymer Science and Engineering,
China University of Science and Technology,
Hefei, China

Jinchuan Yang and Jimmy W. Mays
Department of Chemistry,
University of Alabama at Birmingham,
Birmingham, Alabama, USA

Poly(ε-caprolactone) was characterized by size exclusion chromatography on-line with a right-angle laser-light scattering photometer and a four-capillary bridge design differential viscometer (SEC/RI/RALLS/DV) in tetrahydrofuran (THF) at 25°C. The dependence of intrinsic viscosity and radius of gyration of poly(ε-caprolactone) on molecular weight was established, and Flory's characteristic ratio C_∞ *was calculated for this polymer from these data. The results show that THF is a good solvent for poly(ε-caprolactone). Poly(ε-caprolactone) exhibits a random-coil conformation in THF, and SEC with online RALLS and DV detectors offer an easy way to obtain information on chain*

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Address correspondence to Jimmy W. Mays, Department of Chemistry, University of Tennessee, Chemical Sciences Division, Oak Ridge National Laboratory, 552 Buehler Hall, Knoxville, TN 37996, USA. E-mail: jimmymays@utk.edu

flexibility. The C_∞ *results are in good accord with previously reported values for this polymer.*

Keywords: Multi-detector SEC; Poly(ε-caprolactone); Mark-Houwink-Sakurada (MHS) equation; Radius of gyration; Molecular weight; Flory's characteristic ratio C_∞

INTRODUCTION

Poly(ε-caprolactone) (PCL) is widely employed in pharmaceutical applications, polymer blends, and copolymers that exhibit unique properties. These applications include controlled release of steroids from films and capsules of homopolymers and copolymers of ε-caprolactone[1]. Also, the addition of poly(vinyl butyral), poly(vinyl formal), or poly(vinyl chloride) to PCL induces "banding" (occurrence of ringed extinction patterns) in spherulites of this host polymer over a range of crystallization temperatures[2]. Furthermore, the miscibility and crystallization behavior of poly(ε-caprolactone) with ethylene terephthalate-caprolactone copolyesters (TCL) have been studied[3].

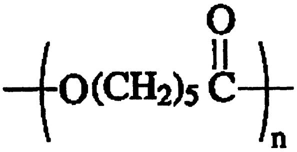
There are relatively few studies published on the dilute solution properties of PCL[4–6]. Koleske and Lundberg[4] measured intrinsic viscosities in benzene and dimethylformamide for fractions of PCL prepared by a dibutylzinc-catalyzed bulk polymerization. Knecht and Elias[5] conducted classical light scattering, osmometry, and viscometry experiments on PCL in various solvents as a function of temperature. Jones et al.[6] reported intrinsic viscosities for PCL in three solvents, as well as dielectric increments and dipole moments. The collective data reported by these authors yield values of Flory's characteristic ratio C_∞[7] ranging from 4.3 to 5.9. Theoretical estimates of C_∞ for PCL are near 6[7].

In this article, we report the solution behavior of poly(ε-caprolactone) in tetrahydrofuran (THF) at 25°C by using size exclusion chromatography with a refractive index concentration detector (SEC/RI), coupled with a right-angle laser-light scattering photometer and a differential viscometer (SEC/RI/RALLS/DV). This triple-detector technique allows molecular weights to be determined directly without resorting to a conventional calibration curve. This is significant because direct calibration can be a complicated matter. SEC calibration curves vary strongly with polymer architecture, and for most commercial polymers direct molecular weight calibration is not possible due to the lack of known molecular weight standards with narrow molecular weight distributions and the same chemical composition as the samples to be investigated. Therefore, in most cases, only relative molecular weight information is obtained from conventional SEC. The multi-detector SEC technique avoids the calibration problems in conventional SEC. The RI detector gives the concentration of polymer at each retention volume, the DV detector measures the imbalance in flow through the four capillaries containing pure solvent and the dilute polymer solution arranged in a Wheatstone bridge configuration[8–10] and gives the intrinsic viscosity, and the RALLS detector determines the molecular weight across the SEC chromatogram[10,11]. The enhanced capabilities and reliability of the multi-detector SEC system have been reported elsewhere[8,9,12–15]. With the use of this technique, the Mark-Houwink-Sakurada (MHS) equation for PCL was determined. The radius of gyration versus molecular weight relationship also was established. From these data, C_∞ was evaluated for PCL and compared with previously reported data for this polymer.

EXPERIMENTAL

Samples

Standard samples of polystyrene used for calibration were supplied by American Polymer Standards Corp. (Mentor, Ohio). Poly(ε-caprolactone) samples used in this study were supplied by Scientific Polymer Products Inc. (Ontario, N.Y.). The structure is as follows:



$$\left[O(CH_2)_5 \overset{O}{\overset{\|}{C}} \right]_n$$

Size Exclusion Chromatography

A dual detector (Model T60) in series with RALLS and DV (Viscotek Corp., Houston, Tex.) was combined on-line with a differential refractometer (RI, Model 410, Waters Corp., Milford, Mass.) coupled to a programmable HPLC pump (Model 590, Waters Corp.). Two size exclusion chromatographic columns (American Polymer Standards Corp.), measuring 30 cm in length, packed with 5 μm diameter polystyrene (PS) gel were in series. Tetrahydrofuran (THF) at a flow rate of 1.0 mL/min was used as the mobile phase and was treated with a supersonic device before use. The samples were dissolved in THF and were filtered with Millex-FG 0.2 μm membrane filter (Millipore Corp., Milford, Mass.). Measurements were performed at 25°C and injection volumes were 100 µL. Viscotek's TriSEC software (Version 3) was used to treat the data obtained. The method used for calibrating interdetector volumes employs a narrow standard of known molecular weight and concentration. The TriSEC software monitors the elution times of the three detectors and adjusts the volume calculation according to the RI detector. This allows for all of the signals to co-elute when the sample has no or narrow polydispersity. The volumes between RALLS and RI (V_{Lapp}) and DV and RI (V_{Vapp}) being calibrated are $V_{Lapp} = V_{Loff} + V_{Lpoly}$ and $V_{Vapp} = V_{Voff} + V_{Vpoly}$ respectively, which contain the terms caused by interdetector volumes of the RALLS and RI (V_{Loff}), and DV and RI (V_{Voff}), as well as the terms caused by sample polydispersity (V_{Lpoly} and V_{Vpoly}). The over-calibrated part was compensated by a known broad polydispersity standard sample.

RESULTS AND DISCUSSION

Characterization of PCL

Table I shows the characterization data obtained for PCL via multi-detector and conventional SEC, from which it is clear that the molecular weights obtained via multi-detector SEC are smaller than those obtained via conventional SEC. Log $[\eta]$ versus retention volume and log M versus retention volume are plotted in Figures 1 and 2, respectively. Figure 1 shows that the intrinsic viscosity $[\eta]$ of PCL is larger than that of PS standard samples having the same hydrodynamic volume. At the same hydrodynamic volume, the molecular weight of PCL is smaller than that of PS standard samples, as shown in Figure 2. Furthermore, Figure 2 shows that the application of conventional SEC with PS calibration would give quite misleading results for molecular weights of PCL (see Table I). Log-log plots of weight average data of $[\eta]$ versus molecular weight (M) and radius of gyration (R_g) versus M are presented in Figures 3 and 4, respectively. The Mark-Houwink-Sakurada MHS equation derived from the data in Figure 3 is as follows:

$$[\eta]_w = 2.90 \times 10^{-4}\ M_w^{0.70} \tag{1}$$

($4500 < M_w < 30{,}000$, correlation coefficient $= 0.988$)

Support for THF being a good solvent for PCL can be inferred from the exponent α of the MHS equation. The power law exponent v and prefactor K' relating radius of gyration and M can be derived from the data in Figure 4. The resulting relationship for PCL in THF at 25°C is as follows:

$$R_{gw} = 2.46 \times 10^{-2}\ M_w^{0.55} \tag{2}$$

($4500 < M_w < 30{,}000$, correlation coefficient $= 0.997$)

TABLE I Characterization data for PCL via multi-detector (M) and conventional (C) SEC

Sample	Method	M_n[a] $\times 10^{-4}$	M_w[b] $\times 10^{-4}$	M_z[c] $\times 10^{-4}$	Pd[d]	$[\eta]_n$[e] (dL/g)	$[\eta]_w$[f] (dL/g)	$[\eta]_z$[g] (dL/g)	R_{gn}[h] (nm)	R_{gw}[i] (nm)	R_{gz}[j] (nm)	Rv[k] (nm)
PCL-A	M	0.40	0.45	0.51	—	0.096	0.108	0.122	2.41	2.56	2.71	1.97
	C	0.39	0.62	0.86	1.60	—	—	—	—	—	—	
PCL-B	M	0.56	0.75	0.97	—	0.124	0.141	0.159	2.99	3.27	3.55	2.56
	C	0.68	1.03	1.39	1.52	—	—	—	—	—	—	
PCL-C	M	0.68	0.84	1.05	—	0.140	0.164	0.190	3.31	3.59	3.87	2.79
	C	0.75	1.30	3.89	1.74	—	—	—	—	—	—	
PCL-D	M	0.66	0.93	1.21	—	0.161	0.189	0.215	3.48	3.87	4.24	3.03
	C	0.94	1.66	2.33	1.76	—	—	—	—	—	—	
PCL-E	M	0.89	1.26	1.63	—	0.197	0.235	0.270	4.11	4.61	5.05	3.61
	C	1.15	2.23	3.23	1.94	—	—	—	—	—	—	
PCL-F	M	1.66	2.70	3.79	—	0.296	0.386	0.471	5.90	6.93	7.87	5.49
	C	2.05	5.12	8.70	2.50	—	—	—	—	—	—	
PCL-G	M	1.57	3.00	4.59	—	0.289	0.388	0.482	5.85	7.12	8.30	5.69
	C	1.97	5.37	9.45	2.73	—	—	—	—	—	—	

[a] Number-average molecular weight.

[b] Weight-average molecular weight.

[c] Z-average molecular weight.

[d] Polydispersity index, M_w/M_n.

[e] Number-average intrinsic viscosity.

[f] Weight-average intrinsic viscosity.

[g] Z-average intrinsic viscosity.

[h] Number-average radius of gyration.

[i] Weight-average radius of gyration.

[j] Z-average radius of gyration.

[k] Viscometric radius.

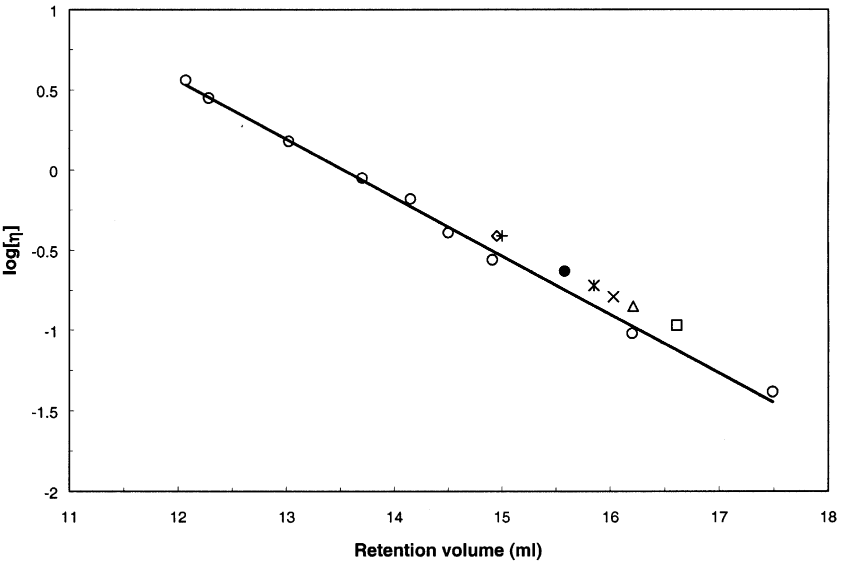


FIGURE 1 Log [η] as a function of retention volume. PS: ○; PCL-A: □; PCL-B: △; PCL-C: ×; PCL-D: ⋇; PCL-E: ●; PCL-F: +; PCL-G: ◇ .

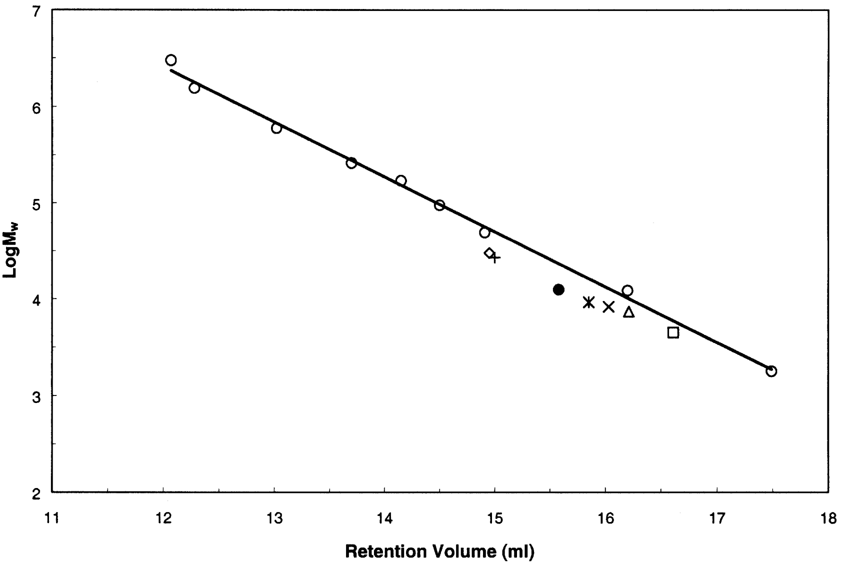


FIGURE 2 Log M as a function of retention volume. PS: ○; PCL-A: □; PCL-B: △; PCL-C: ×; PCL-D: ⋇; PCL-E: ●; PCL-F: +; PCL-G: ◇ .

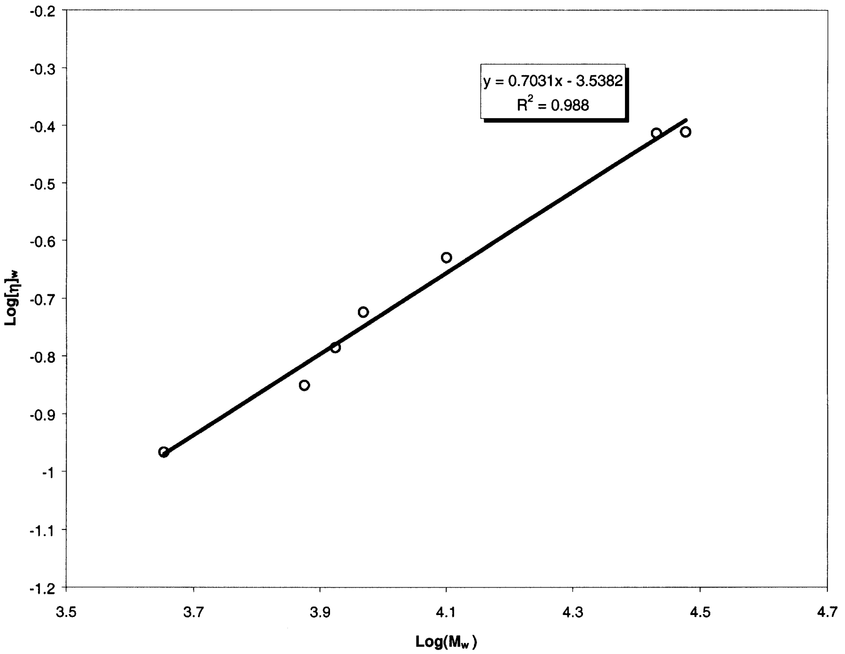


FIGURE 3 Log [η] as a function of log M for PCL.

Information concerning the conformation of polymer chains can also be inferred from radius of gyration versus molecular weight plot. The slope of 0.55 obtained falls between 0.5 and 0.6, which corresponds to linear random coils in the good solvent and theta solvent limit, respectively. This suggests that PCL in THF at 25°C exists as a solvent-swollen random coil. These [η] and R_g data support the large positive second virial coefficients reported previously by Knecht and Elias[5] for the PCL/THF system via light scattering. Furthermore, the viscometric radius, R_V, is calculated from the expression[21]

$$R_V = ([\eta]M_w)^{1/3}(10/3\pi N_A)^{-1/3} \tag{3}$$

where N_A is Avogadros constant and R_V values are listed in Table I.

A log-log plot of R_V versus M_w is shown in Figure 5, and the following power law is obtained:

$$R_V = 1.66 \times 10^{-2}\ M_w^{0.57} \tag{4}$$

($4500 < M_w < 30{,}000$, correlation coefficient $= 0.998$)

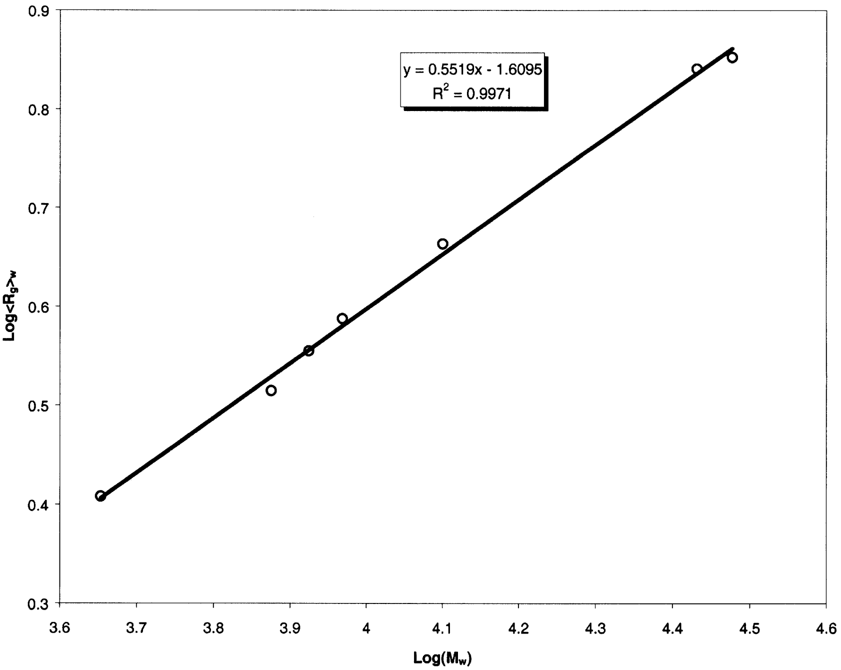


FIGURE 4 Log R_g as a function of log M for PCL.

Flory's Characteristic Ratio C_∞

Chain flexibility refers to the activation energies required to activate vibrational and rotational motions, as a consequence of which different conformations of the chain can be assumed. For random-coil polymers, the most useful and widely used parameter describing conformational flexibility is Flory's characteristic ratio C_∞. There are neither rotational hindrances nor bond-angle restrictions for a freely jointed chain; therefore, C_∞ equals 1 for this model chain. Larger values of C_∞ indicate departure from freely jointed behavior, i.e., diminished flexibility. C_∞ is defined as[7]

$$C_\infty = \lim_{N\to\infty} \frac{\langle r^2\rangle_0}{Nl^2} \tag{5}$$

or rearranged as

$$C_\infty = \lim_{N\to\infty} \frac{\langle r^2\rangle_0/M}{(N'/M_0)l^2} \tag{6}$$

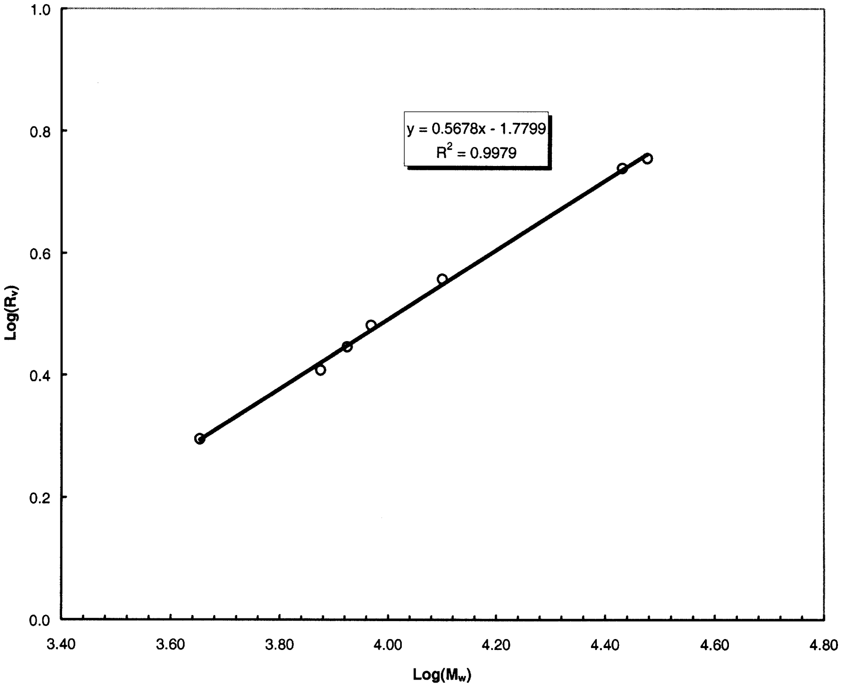


FIGURE 5 Log R_v as a function of Log M_w for PCL.

Here M_0 is molecular weight of the repeating unit (114 for PCL), $\langle r_0^2 \rangle$ is the unperturbed mean-square end-to-end distance of an isolated chain, N is the number of bonds in the main chain, N′ is the number of main chain bonds per repeat unit (seven for PCL), and l is the average main-chain bond length. The conformation of the ester group is planar and predominantly *trans*, and the bond length is shortened from 1.44 (or 1.43) to 1.33 Å as a consequence of the partial double-bond character of the CO–O bonds[16]. Thus,

$$l = [2 \times l(\text{C–O}) + 5 \times l(\text{C–C})]/7 = (1.33 + 1.44 + 1.51 + 1.53 \times 4) = 1.49\,\text{Å}$$

Unperturbed dimensions can be estimated by conducting chain measurements via RALLS or DV measurements in good solvents and then extrapolating to the unperturbed state. THF is a good solvent for PCL as indicated in the previous section. It is well known that the commonly used Burchard-Stockmayer-Fixman (BSF) equation provides reliable estimates of K_θ as long as the excluded volume effects are not too large[17–19]:

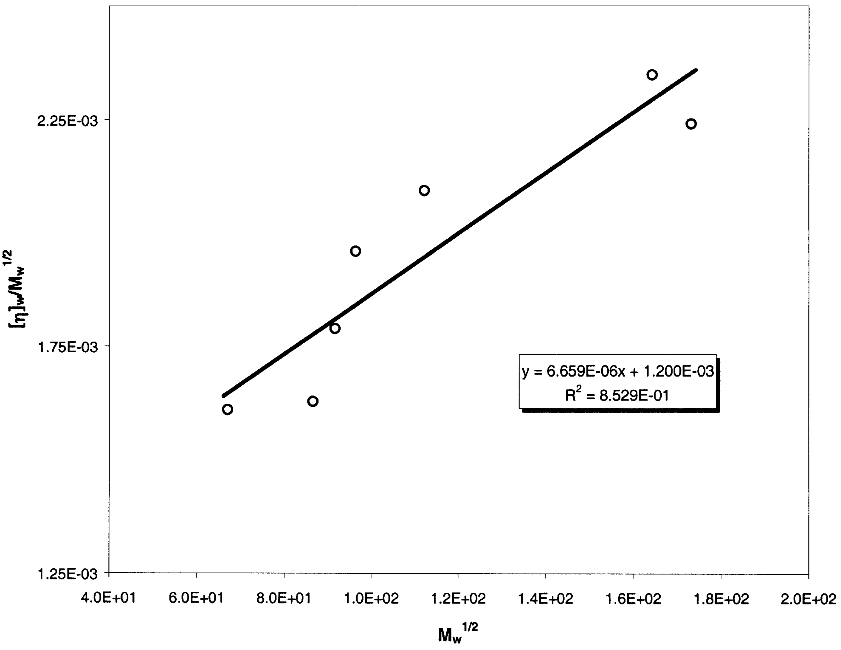


FIGURE 6 Burchard-Stockmayer-Fixman plot for PCL.

$$([\eta]M^{-1/2}) = K_\theta + 0.51\ \Phi_0\ BM^{1/2} \tag{7}$$

where Φ_0 is Flory's "universal viscosity constant" equal to $2.5 \times 10^{21}\,\text{mol}^{-1}$ when the dimensions of $[\eta]_\theta$ (intrinsic viscosity under θ conditions) are dL/g and the unperturbed mean-square end-to-end distance $\langle r^2\rangle_0$ is in cm^2. A plot of $([\eta]M^{-1/2})$ as a function of $M^{1/2}$ was used (Figure 6) to obtain K_θ as the intercept based on the weight average data presented in Table I. The resulting K_θ value is 1.20×10^{-3}.

Under unperturbed condition, the MHS equation can be expressed as follows

$$[\eta]_\theta = K_\theta M^{1/2} \tag{8}$$

which, combined with the Fox-Flory relationship, yields

$$[\eta]_\theta = \frac{\Phi_0 \langle r^2\rangle_0^{3/2}}{M} \tag{9}$$

or

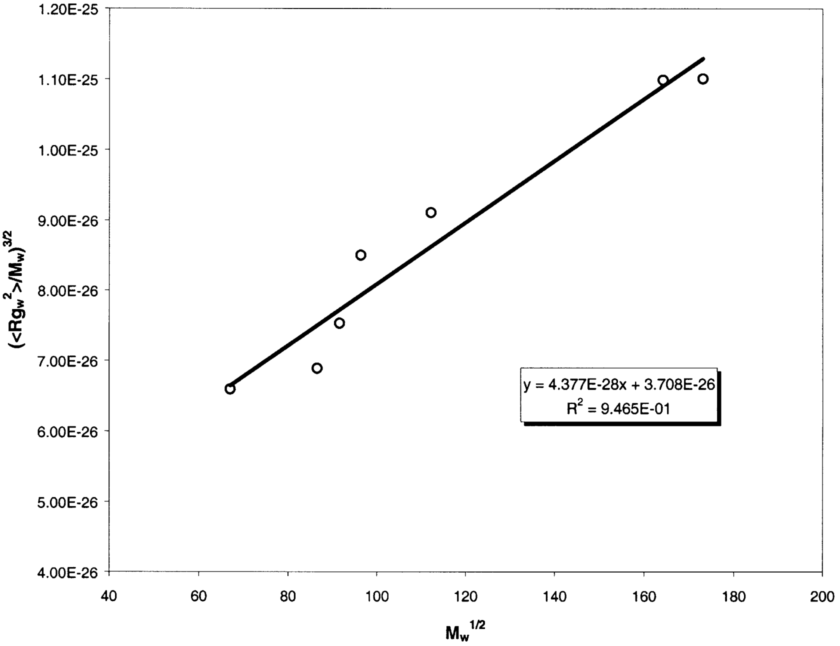


FIGURE 7 Baumann plot for PCL.

$$\frac{\langle r^2\rangle_0}{\mathrm{M}} = \left(\frac{\mathrm{K}_\theta}{\Phi_0}\right)^{2/3} \tag{10}$$

Inserting the value of K_θ and Φ_0 into Equation (10), we obtain $\langle r^2\rangle_0/\mathrm{M} = 6.13 \times 10^{-17}$ $\mathrm{cm^2mol/g}$ and $\mathrm{C}_\infty = 4.5$. By applying the method of Baumann[20] to treat the $\mathrm{R_g}$(z-average) data as a function of molecular weight (weight average) another estimation of C_∞ may be carried out:

$$(\langle \mathrm{R_g^2}\rangle/\mathrm{M})^{3/2} = (\langle \mathrm{R_g^2}\rangle_o/\mathrm{M})^{3/2} + \mathrm{BM}^{1/2} \tag{11}$$

This latter approach yields a value of $\mathrm{C}_\infty = 4.9$ (Figure 7). This value is in good agreement with literature values noted above of 4.3 to 5.9 obtained in different solvents and based upon various measurement techniques. Thus, the multi-detector SEC technique has been shown to yield estimates of C_∞ that are in accord with data generated by much more laborious off-line techniques using fractionated polymers.

CONCLUSION

Multi-detector SEC has been applied to the characterization of PCL in THF at 25°C. This technique allows the relationships between intrinsic viscosity and molecular weight and radius of gyration and molecular weight to be determined, even for low-molecular-weight polymers, without laborious off-line fractionation. Furthermore, these data may be used to estimate thermodynamic interactions in solution and for estimation of chain flexibility. The technique generates a characteristic ratio of 5 (± 0.5) for PCL in agreement with experimental values in the literature.

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