Solution Properties of Poly(*N*-vinylcarbazole) and Its Copolymers with Methyl Methacrylate

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ABSTRACT: Solution properties of poly(*N*-vinylcarbazole) (PVCz) and copolymers of *N*-vinylcarbazole with methyl methacrylate are investigated by using SEC coupled with differential refractive index (RI), multiangle light scattering (MALS), and UV detectors. The technique affords information on molecular weight, molecular weight distributions, and the chemical composition of copolymers. Moreover, the polymer dimensions are investigated in two different solvents, tetrahydrofuran (THF) and toluene, which are good and poor solvents, respectively, for poly(*N*-vinylcarbazole). The collapse of the polymer chain, the scaling laws, unperturbed dimensions, and characteristic ratios are determined by employing only a broad polydisperse polymer sample. The results are in good agreement with those obtained by much more complex procedures for the homopolymer PVCz. The influence of the methyl methacrylate content in the dimensions of the copolymer chains is analyzed. Unperturbed dimensions are also calculated employing a simple two-state RIS model. Agreement between calculated and measured values of C_n is excellent for homopolymers and copolymers with contents of MMA units up to ca. 80%.

Introduction

The use of size exclusion chromatography with multiple detectors has become a habitual way of obtaining quantitative information on molecular weight distributions of polymers.[1,2] The combination of a concentration-based detector, such as the usual refractive index (RI) detector, with a multiangle laser light scattering (MALS) detector is particularly advantageous since it offers the possibility of obtaining both molecular weight and dimensions along the chromatogram.[3] The dimensions are determined through the root-mean-square radius of gyration, which is a very convenient magnitude to express the size of the chain. This is due to the fact that its definition is applicable to macromolecules of any shape and that it can be related to the molecular weight by the scaling relationships.[4] For polymer samples with broad polydispersity, the combination of these two detectors affords a direct way to measure dimensions vs molecular weight over a broad range and thus to gain information about the polymer solution properties in good solvents that can even be extrapolated to unperturbed conditions.[5,6]

The analysis of copolymers is complicated by the fact that the chemical composition can also affect the size of the macromolecule, and thus the heterogeneity of the copolymer may influence the relationship between dimensions and molecular weight. The use of multiple detectors, which may be selective for different polymer structures, has been investigated extensively, since they can afford the measurement of the chemical composition in copolymers.[7−17]

The aim of the present work is to study the solution properties of poly(*N*-vinylcarbazole) (PVCz) and copolymers of *N*-vinylcarbazole with methyl methacrylate by using SEC coupled with three different detectors, namely differential refractive index (RI), multiangle light scattering (MALS), and UV detectors. These polymers present unique photophysical properties[18] that have been studied in solution by some of us.[19,20] Thus, it seemed interesting to complement the study with a different technique. The work consists of two different parts. We first collect the information that the technique affords on molecular weight, molecular weight distributions, and chemical composition of copolymers. Second, the polymer dimensions are investigated in two different solvents, tetrahydrofuran (THF) and toluene, that are good and poor solvents, respectively, for poly(*N*-vinylcarbazole).[21,22] The collapse of the polymer chain, the scaling laws, unperturbed dimensions, and characteristic ratios are determined by using only a few milligrams of a broad polydisperse polymer sample and avoiding tedious fractionation procedures.

Experimental Section

Carbazole Polymers. The polymers were prepared by the free-radical polymerization of mixtures of methyl methacrylate and *N*-vinylcarbazole as described elsewhere.[19] The four copolymers used are presented in Table 1 together with their chemical composition obtained by elemental analysis.[19] Copolymers were named as in the previous work.[19]

Measurements. Size exclusion chromatography measurements were carried out using a Waters Associates SEC equipped with a model 510 pump, a U6K injector, a differential refractive index detector model 410 (RI) and a UV detector model 490E working at wavelengths of 296 and 342 nm for THF and toluene, respectively. The multiangle light scattering detector was a DAWN DSP-F laser photometer from Wyatt Technology Corp. The photometer was calibrated with spectrometric grade toluene, and the normalization of its detectors was performed with standard monodisperse polystyrene of low molecular weight that did not show angular dependence on the light scattering signal. The same polystyrene standard was used to determine the interdetector volumes. Two columns PLgel mixed B (Polymer Laboratories) in series completed the equipment. Tetrahydrofuran (THF) and toluene (Scharlau), freshly distilled from sodium and benzophenone, were used as eluents. The solvents were filtered through a 0.2 μm Fluoropore membrane and degassed. The flow rate used was 1.0 mL/min and the temperature 25 °C.

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Table 1. CarbazoleWeight Fractions, Specific Refractive Indices, Averaged Molecular Weights, Root-Mean-Square Radii, and Polydispersities of Polymers in THF and Toluene

		THF				toluene			
polymer	w_{Cz}	dn/dc (mL/g)	$10^{-6}M_w$ (g/mol)	$\langle s^2\rangle_z^{1/2}$ (nm)	M_w/M_n	dn/dc (mL/g)	$10^{-6}M_w$ (g/mol)	$\langle s^2\rangle_z^{1/2}$ (nm)	M_w/M_n
PVCz	1	0.253	1.04 ± 0.03	52 ± 1	2.4 ± 0.1	0.15	0.92 ± 0.07	35 ± 2	2.1 ± 0.1
P1	0.97	0.248	1.26 ± 0.02	56 ± 1	2.3 ± 0.1	0.15	0.82 ± 0.05	36 ± 3	2.0 ± 0.1
P4	0.51	0.171	2.23 ± 0.04	67 ± 1	1.5 ± 0.1	0.087	3.05 ± 0.08	62 ± 2	1.5 ± 0.1
P7	0.25	0.128	1.48 ± 0.03	65 ± 1	2.0 ± 0.1	0.052	1.69 ± 0.01	56 ± 2	2.1 ± 0.1
P9	0.08	0.099	2.1 ± 0.2	83 ± 5	1.9 ± 0.2	0.029	2.16 ± 0.01	54 ± 3	1.7 ± 0.1

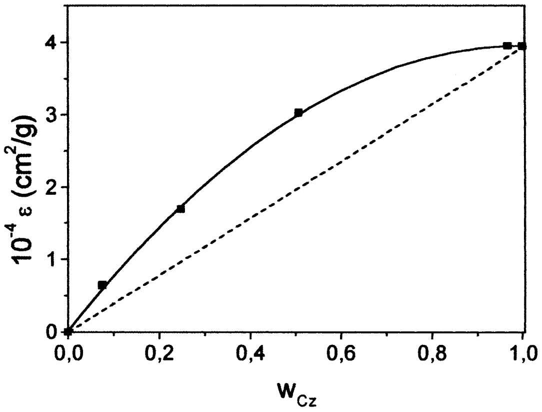

Figure 1. Absorption coefficients at 296 nm for PVCz and copolymers in THF as a function of the carbazole weight content. The broken line represents an hypothetical linear variation of ϵ with w_{Cz}.

The absorption coefficients, ϵ, of the polymers in THF at 296 nm were measured in a UNICAM 8625 UV spectrophotometer, and they are depicted as a function of the carbazole weight fraction in Figure 1. It is important to point out that the dependence of ϵ for copolymers is not linear on the fraction of carbazole units, as is usually assumed.[23] This discrepancy will be explained later.

Care had to be taken when preparing the solutions of the homopolymer poly(*N*-vinylcarbazole) (PVCz) and copolymer P1 in toluene. Toluene is a Θ solvent for PVCz at 37 °C and is therefore a poor solvent at the temperature of the measurements, 25 °C. The solutions were warmed to 35 °C for several hours in order to obtain homogeneous solutions, filtered, and then cooled to 25 °C without any precipitation being noticed.

The MALS detector simultaneously measures the excess Rayleigh ratio at different θ angles and permits the calculation of the weight-average molecular weight, M_w, and the mean-square radius of gyration, $\langle s^2\rangle$, for each slice across a sample peak of the size exclusion chromatogram according to the basic equation[3,24]

$$\frac{Kc}{\Delta R_\theta} = \frac{K'\left(\frac{dn}{dc}\right)^2 c}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_z \sin^2\left(\frac{\theta}{2}\right) + ...\right) \quad (1)$$

where ΔR_θ is the excess Rayleigh ratio at angle of observation θ, λ is the light wavelength in the solution, and K represents the optical constant that is related to the wavelength in vacuo, λ_0, the solvent refraction index, n, Avogadros'number, N_A, and the solution refraction index increment, dn/dc, by

$$K = \frac{4\pi^2 n^2}{\lambda_0^{\,4} N_A}\left(\frac{dn}{dc}\right)^2 \quad (2)$$

Considering the slices of the chromatogram to be monodisperse, the different averages over M and $\langle s^2\rangle$ are the same, and thus M_w and $\langle s^2\rangle_z$ represent the molecular weight and the mean-square radius of gyration of the slice, M_i and $\langle s^2\rangle_i$, respectively.

The ASTRA 4.73 software (Wyatt Technology Corp.) was used in the computation of molecular weights and radii of gyration.

Determination of the Chemical Composition of the Copolymers. Two different methods have been used. The first one uses the relationship between molecular weights obtained with MALS when using RI or UV as the concentration detector. This method has been applied to copolymers of styrene and methyl methacrylate[17] and offers good results in a very simple manner if the copolymers are homogeneous. The second is the more traditional way, based on the differences in the signals of the RI and UV, which has been modified in order to take into account the nonlinearity of the absorption coefficients.

First Method. The signal of the RI detector for a slice i is proportional to the polymer concentration in the slice, c_i, and to the refractive index increment

$$S_i^{RI} = k^{RI} c_i \left(\frac{dn}{dc}\right)_i \quad (3)$$

where k^{RI} is the response factor of the detector. When using the RI detector, the molecular weight calculated using eq 1 with the value of dn/dc for the whole sample and extrapolated to zero angle would be

$$M_i^{RI} = \frac{(\Delta R_\theta)_i}{K'\left(\frac{dn}{dc}\right) c_i \left(\frac{dn}{dc}\right)_i} \quad (4)$$

If the (dn/dc)$_i$ for the slice coincides with the dn/dc of the whole sample, M_i will be the true molecular weight. If this condition is not fulfilled, an apparent molecular weight will be obtained. Homopolymers and random copolymers are assumed homogeneous from the chemical composition point of view (see subsequent results and discussion). Therefore, the differences in the values of (dn/dc)$_i$ for the different slices will only be due to differences in molecular weight that are negligible in the range of molecular weight studied in this work. Thus

$$M_i^{RI} = \frac{(\Delta R_\theta)_i}{K'\left(\frac{dn}{dc}\right)^2 c_i} \quad (5)$$

The UV detector signal for the ith slice will be proportional to the concentration of the polymer in the slice through

$$S_i^{UV} = k^{UV} l \epsilon c_i \quad (6)$$

where k^{UV} and l are the response factor and the cell path length of the instrument, respectively, and ϵ is the absorption coefficient of the polymer.

For homogeneous copolymers with repeating units A and B, if the UV detector is used at a wavelength for which only one component, ca. A, absorbs, the signal of the detector is proportional to the amount of A units, and the signal for the copolymer can be expressed as

$$S_i^{UV} = k^{UV} l \epsilon_A c_i (w_A)_i \quad (7)$$

where ϵ_A is the absorption coefficient of the homopolymer A, c_i the concentration of the copolymer, and $(w_A)_i$ the weight fraction of A units in the slice. Assuming, as is usual, that the absorption coefficient does not vary with the copolymer composition, the product $k_A^{UV} = k^{UV} l \epsilon_A$ is the response factor of UV for polymer A. Thus, using the same UV response factor for homo- and copolymers, the concentration that the detector senses will be $c_i(w_A)_i$, and the apparent molecular weight calculated using eq 1 with the value of d*n*/d*c* for the whole sample and extrapolated to zero angle would be

$$M_i^{UV} = \frac{(\Delta R_\theta)_i}{K'\left(\frac{dn}{dc}\right)^2 c_i (w_A)_i} \tag{8}$$

Thus, the ratio of apparent molecular weights M_i^{RI}/M_i^{UV} may be expressed as

$$\frac{M_i^{RI}}{M_i^{UV}} = (w_A)_i \tag{9}$$

and affords a very simple way to obtain random copolymer compositions.[17] It is obvious that for a homopolymer $M_i^{RI} = M_i^{UV}$ whereas for a random copolymer $M_i^{RI}/M_i^{UV} = w_A$ since as stated above they are homogeneous polymers.

However, the assumption that the absorption coefficient of the A units does not vary with the copolymer composition[17] is not valid for the copolymers studied in this work and, as stated above, for the present copolymers

$$\epsilon \neq \epsilon_{linear} = \epsilon_{PVCz} w_{Cz} \tag{10}$$

where ϵ_{PVCz} is the absorption coefficient of the homopolymer. Therefore, eq 9 has to be corrected.

Second Method. A standard procedure to obtain the chemical composition of copolymers is based in the comparison of the responses of UV and RI SEC detectors.[7–9,25] The procedure was modified in order to take into account the fact that the absorption coefficient of the copolymers of this work is not linear in the composition (eq 10), and the following relationships are deduced. The ratio of the signals of the UV and RI SEC detectors for slice *i* can be expressed by combining eqs 3 and 6 as

$$R_i = \frac{S_i^{UV}}{S_i^{RI}} = \frac{k^{UV} l \epsilon c_i}{k^{RI}\left(\frac{dn}{dc}\right)_i c_i} = \frac{k^{UV} l \epsilon}{k^{RI}\left(\frac{dn}{dc}\right)} \tag{11}$$

Thus, the value of R_i should be constant through the chromatogram for homogeneous polymers.

Taking into account that the d*n*/d*c* of a copolymer may be expressed as

$$\left(\frac{dn}{dc}\right)_{copol} = (1 - w_{Cz})\left(\frac{dn}{dc}\right)_{PMMA} + w_{Cz}\left(\frac{dn}{dc}\right)_{PVCz} \tag{12}$$

the relationship between the signal ratios for homo and copolymers can be expressed as

$$\frac{R_i^{Copol}}{R_i^{PVCz}} = \frac{\epsilon_{copol}\left(\frac{dn}{dc}\right)_{PVCz}}{\epsilon_{PVCz}\left(\frac{dn}{dc}\right)_{copol}} = \frac{\epsilon_{copol}\left(\frac{dn}{dc}\right)_{PVCz}}{\epsilon_{PVCz}\left[(1 - (w_{Cz})_i)\left(\frac{dn}{dc}\right)_{PMM} + (w_{Cz})_i\left(\frac{dn}{dc}\right)_{PVCz}\right]} \tag{13}$$

and thus, the carbazole weight fraction at elution point *i* can be obtained by using

$$(w_{Cz})_i = \frac{\left[\frac{R_i^{PVCz}}{R_i^{Copol}}\frac{\epsilon_{copol}}{\epsilon_{PVCz}}\left(\frac{dn}{dc}\right)_{PVCz}\right] - \left(\frac{dn}{dc}\right)_{PMMA}}{\left[\left(\frac{dn}{dc}\right)_{PVCz} - \left(\frac{dn}{dc}\right)_{PMMA}\right]} \tag{14}$$

It is important to notice that although ϵ_{copol} varies with composition in a nonlinear way (see Figure 1), experimental values of this magnitude were obtained for all the studied samples (solid squares in Figure 1) and employed in eq 14, assuming that they are constant throughout the whole chromatogram of each copolymer which would be a good approximation provided that the composition does not change with elution volume.

Results and Discussion

Molecular Weight Distributions. Figures 2 and 3 show the signals of the RI and UV detectors and one of the MALS detectors (at 90° scattering angle) of the SEC chromatograms for the polymers in THF and toluene, respectively. The light scattering signal is proportional to the product of molecular weight and concentration and consequently has a different shape than that of the RI and UV signals that are proportional to concentration. The PVCz chromatogram in THF shows a reproducible small peak at low elution volume that disappears for copolymers with higher MMA content and that does not appear in toluene. It has been reported[26] that cationic polymerization can occur simultaneously with free radical polymerization, yielding bimodal chromatograms. The values of averaged molecular weights and radii of gyration presented in Table 1 are obtained with the whole chromatogram. For the computation of chemical composition and scaling laws, however, the small peak was not taken into account in order to be sure of the homogeneity of the polymers. As we were under θ conditions, the process of the solution of PVCz and P1 in toluene was difficult, and the peak at high elution values that appears can be due to some degradation of the sample. Moreover, the precision of measurements in toluene decreases as the values of d*n*/d*c* of the polymers in toluene are much smaller than in THF. Methyl methacrylate is nearly isorefractive with toluene, and thus copolymers with a high MMA content yield signals of low intensity in the detectors, as can be seen in Figure 3. These facts will also explain the slight differences in the molecular weight averages for the polymers in both solvents.

Figure 4 presents the molecular weight distributions of the polymers calculated from the combined measurements in THF, of molecular weight and concentration. Table 1 depicts the averaged molecular weights and polydispersities for the polymers in the two solvents studied.

Chemical Composition. Figure 5 presents the relationship between molecular weight and the elution volume, i.e., the molecular weight calibration curves, in THF obtained with the RI (eq 5) or UV (eq 8) as concentration detectors and the ratio M_i^{RI}/M_i^{UV}. This ratio is constant throughout the chromatogram, indicating that the assumption of homogeneous composition of the polymers is correct. As expected, the coincidence of the molecular weight calibration curves obtained with the two detectors is perfect for the homopolymer PVCz, and thus the values of the ratio M_i^{RI}/M_i^{UV} are the unity. Table 2 presents the average values of M_i^{RI}/M_i^{UV} for the part of chromatogram that corresponds to linear mo-

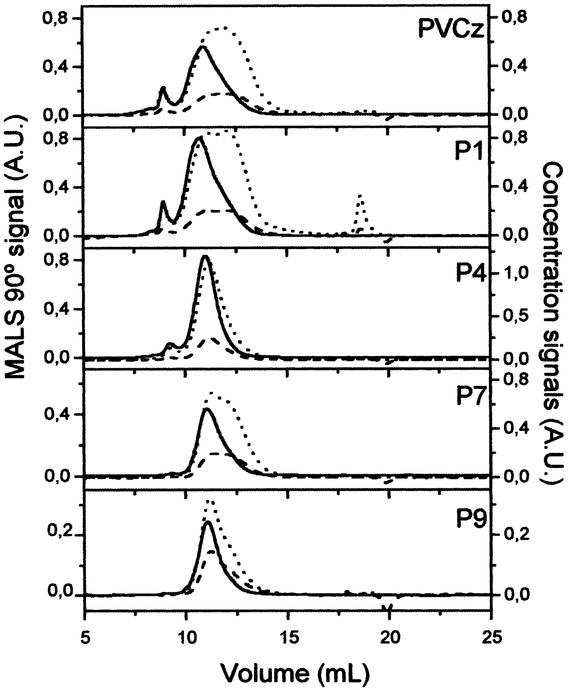

Figure 2. Chromatograms showing the MALS signal at 90° (solid line), the RI signal (dashed line), and the UV signal (dotted line) obtained for PVCz and copolymers in THF.

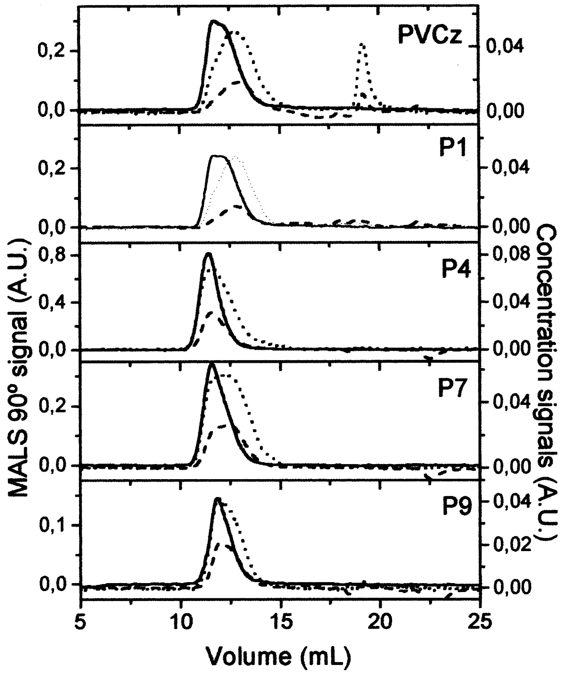

Figure 3. Chromatograms showing the MALS signal at 90° (solid line), the RI signal (dashed line), and the UV signal (dotted line) obtained for PVCz and copolymers in toluene.

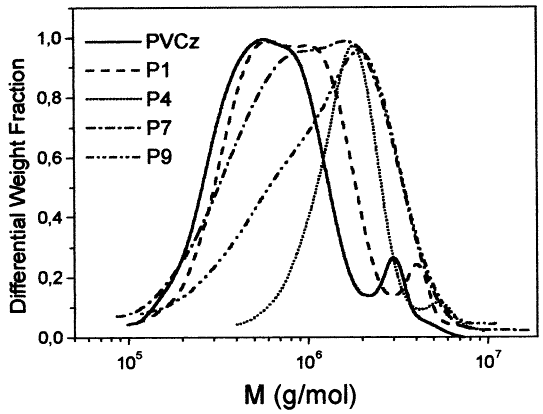

Figure 4. Molecular weight distributions of PVCz and copolymers.

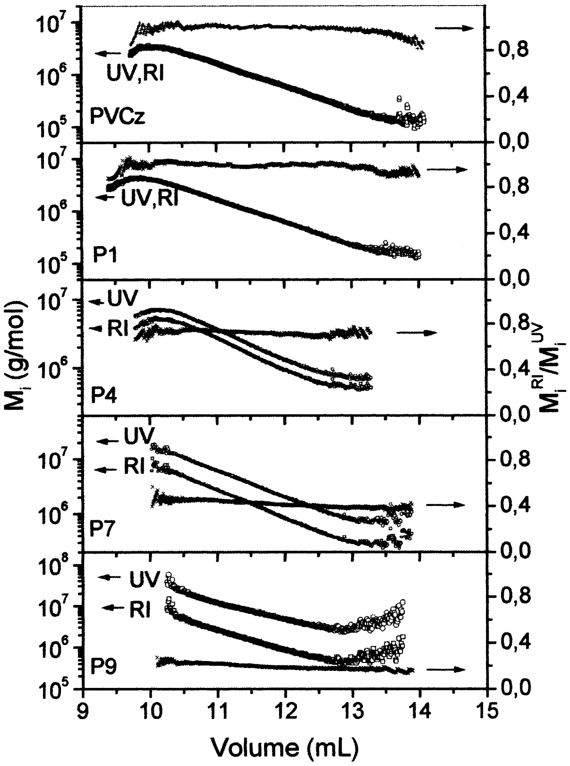

Figure 5. Log plot of molecular weight vs elution volume obtained using RI (☐) and UV (■) detectors and their ratio, $M_i^{\mathrm{RI}}/M_i^{\mathrm{UV}}$ (×) in THF for PVCz and copolymers.

Table 2. Chemical Compositions of Copolymers

polymer	$\langle M_i^{\mathrm{RI}}/M_i^{\mathrm{UV}}\rangle$	$\epsilon_{\mathrm{linear}}/\epsilon$	w_{Cz}	$\langle R_i\rangle$	w_{Cz}(eq 14)
PVCz	1.00 ± 0.01	1	1	4.13 ± 0.04	1
P1	0.99 ± 0.01	0.97	0.96 ± 0.1	4.20 ± 0.05	0.97 ± 0.01
P4	0.72 ± 0.02	0.66	0.48 ± 0.1	4.4 ± 0.1	0.56 ± 0.02
P7	0.42 ± 0.09	0.58	0.24 ± 0.1	3.4 ± 0.2	0.26 ± 0.05
P9	0.19 ± 0.02	0.46	0.09 ± 0.2	2.1 ± 0.3	0 ± 0.1

lecular weight calibration curves. Thus, the head and tail of the chromatograms which, as can be seen in Figure 5, have less precision have not been used in the calculations. As stated above (eq 10), the values of the ratio $M_i^{\mathrm{RI}}/M_i^{\mathrm{UV}}$ for copolymers are not equal to the weight fraction of carbazole. This discrepancy is due to the unique characteristics of the carbazole group. The dependence of ϵ on the fraction of carbazole units for copolymers is not linear (Figure 1), as could be expected looking at the results on copolymers containing other chromophores.[17] The carbazole group is sterically very bulky, and its accommodation in a vinyl homopolymer chain can only be envisaged with a certain amount of interactions between neighboring carbazoles.[27] Such interferences among carbazole groups are manifested by ^{1}H MNR[28,29] and ^{13}C MNR spectra,[30,31] and it is also apparently evidenced in the abnormal values of absorption coefficients of carbazole groups when forming part of the chain. Any attempt in determining the copolymer compositions based directly of absorption spectrum[32]

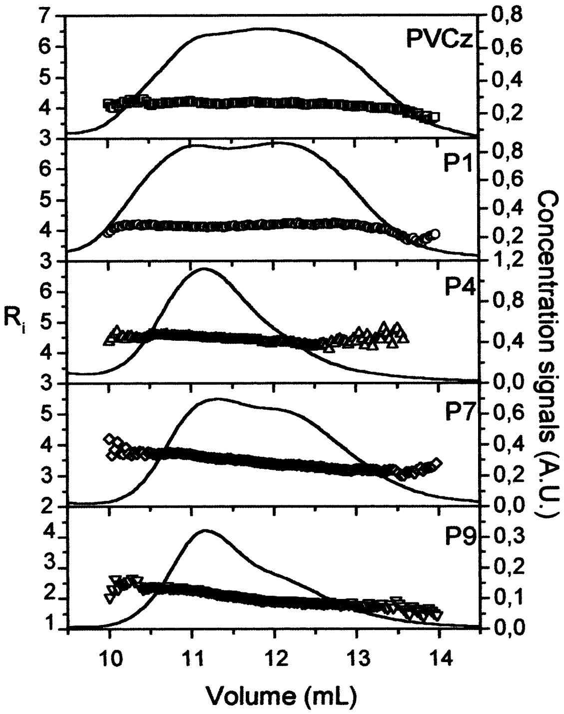

Figure 6. Ratio of the signals of UV and RI detectors for PVCz and copolymers. Solid lines indicate the signals from the RI detector.

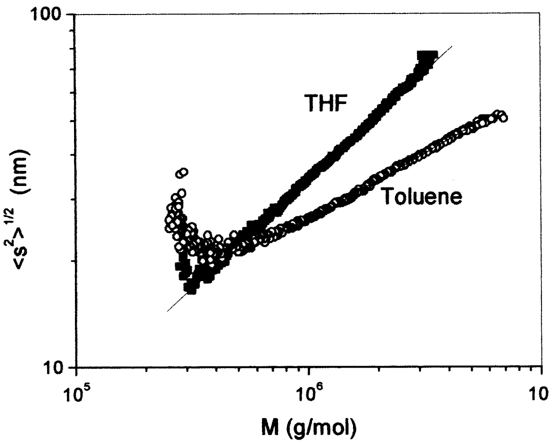

Figure 7. A log−log plot of root-mean-squared radius of gyration vs molecular weight for PVCz in THF (■) and toluene (□).

leads to values which by wrong values which are different from those obtained by elemental analysis. Thus, the values of $M_i^{\mathrm{RI}}/M_i^{\mathrm{UV}}$ must be corrected by the factor $\epsilon_{\mathrm{linear}}/\epsilon$ (Table 2) where $\epsilon_{\mathrm{linear}}$ is given by eq 10 and represented by a broken line in Figure 1. The corresponding values of the weight fractions are presented in the fourth column of Table 2 and are in very good agreement with the weight fractions calculated through elemental analysis (Table 1).

The use of the second method to determine the chemical composition requires the calculation of the values of the ratio of UV/RI signals for the polymers, R_i (eq 13), which are shown in Figure 6. This magnitude provides a more traditional form to obtain chemical composition. With homopolymers and chemically homogeneous copolymers R_i should not depend on the slice of the chromatogram and should be a constant for the whole peak. However, several recent works show that different factors such as interdetector delay, baseline selection, and nonlinearity of the detector response[33−36] can increase the error in the polymer analysis. The comparison of Figures 5 and 6 shows that the deviations for the R_i values of different slices are larger than the deviations for the $M_i^{\mathrm{RI}}/M_i^{\mathrm{UV}}$ values of the first method. Mean values of this magnitude for the central part of the chromatogram and the corresponding weight fractions, obtained with this method using eq 14, are presented in the two last columns of Table 2

Chain Dimensions. The size and the mass of a macromolecule are related through different relationships that are called scaling laws[37] and can be expressed as $\langle s^2\rangle^{1/2} = QM^q$. The scaling law exponent q depends on the conformations of the molecule, and for random coil polymers it also depends on the thermodynamic quality of the solvent. Thus, for θ conditions the excluded volume is zero, and the root-mean-square radius of gyration $\langle s^2\rangle^{1/2}$ scales with molecular weight in the random walk manner $\langle s^2\rangle^{1/2} \propto M^{1/2}$, whereas for very good solvents the excluded volume has to be taken into account and the exponent q approximates 0.6. Below the θ temperature the interactions between polymer segments become attractive, and the chains shrink very fast assuming a globular shape with $\langle s^2\rangle^{1/2} \propto M^{1/3}$. Thus, relating the dimensions (radius of gyration) and the molecular weight of the polymer chains affords information on the shape of the polymers. The use of a multiangle light scattering detector enables the evaluation of both the weight-average molecular weight M_{w} and the mean-square radius of gyration, $\langle s^2\rangle_z$, for each slice across a sample peak of the size exclusion chromatogram. Considering the slices of the chromatogram as monodisperse samples, the different averages over M and $\langle s^2\rangle$ are the same, and thus, no correction for polydispersity is required. Therefore, the parameters Q and q of the scaling law can be obtained with just one sample of a polydisperse polymer.[5]

Figure 7 shows the log−log plot of the radius of gyration vs molecular weight for PVCz in both THF and toluene solvents. The differences between the thermodynamic quality of both solvents are easily noticed. THF is a good solvent, and therefore the dimensions of chains of similar molecular weight are bigger than in toluene, which is a poor solvent. For THF, the plot is linear in the whole range of molecular weights. The dispersion of the points for values of radius of gyration lower than 20 nm is due to the increase of the error in the determination of this magnitude as the molecules approximate isotropic scattering behavior and the angular dependence of scattered light diminishes. However, the plot for toluene shows a pronounced curvature at low molecular weights. Similar curvatures had been reported for polystyrene gels[3] and for other polymers,[38−41] and in this case it can be related to the $T < \theta$ conditions of the polymer. The slope of the plots provides $q = 0.61 \pm 0.01$ and 0.38 ± 0.02 for THF and toluene, respectively (see Table 3), in very good agreement with the thermodynamic quality of the solvents.

For copolymer P1, the scaling laws are similar to those of the homopolymer and they have not been depicted. The corresponding Q and q parameters are shown in Table 3. The three copolymers with higher MMA content also have very similar scaling laws among them although very different from those of homopolymer and copolymer P1. The scaling laws for one of them, copolymer P7, are shown in Figure 8. The parameters

Table 3. Scaling Parameters, Unperturbed Dimensions, Characteristic Ratio, and Number Average Length of Sequences MMA

	10^2Q		q				
polymer	THF	toluene	THF	toluene	$10^4\langle s^2\rangle_0/M$	C_n	$\langle n_{MMA}\rangle$
PVCz	0.72 ± 0.02	16.2 ± 0.1	0.61 ± 0.01	0.38 ± 0.02	6.5 ± 0.1	15.9 ± 0.2	0.00
P1	0.80 ± 0.09	16.6 ± 0.1	0.60 ± 0.02	0.37 ± 0.03	7.1 ± 0.3	16.9 ± 0.6	0.49
P4	0.98 ± 0.08	2.35 ± 0.03	0.57 ± 0.02	0.51 ± 0.02	8.7 ± 0.1	14.6 ± 0.2	2.66
P7	1.16 ± 0.05	2.88 ± 0.02	0.58 ± 0.01	0.50 ± 0.02	10.0 ± 0.2	14.5 ± 0.3	6.12
P9	1.13 ± 0.05	3.72 ± 0.04	0.57 ± 0.02	0.49 ± 0.02	11.0 ± 0.2	14.4 ± 0.3	22.6
PMMA[a]	0.869 ± 0.05		0.59 ± 0.01		7.0 ± 0.2	8.8 ± 0.3	∞

[a] Taken from ref 5.

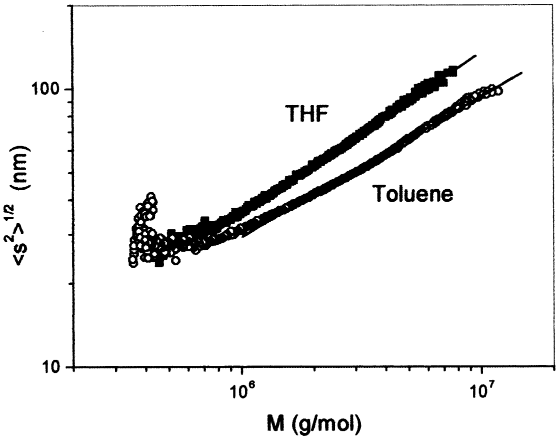

Figure 8. A log−log plot of root-mean-squared radius of gyration vs molecular weight for copolymer P7 in THF (■) and toluene (□).

Q and *q* for the three copolymers are presented in Table 3. THF is also a good solvent for the three copolymers as the values of the scaling law exponent *q* are very close to 0.6. On the contrary, toluene is a θ solvent for the three copolymers since the values of the *q* parameter are very close to 0.5. Toluene is a good solvent for PMMA; thus, the presence of significant amounts of MMA units in the copolymers P4, P7, and P9 improves the quality of the solvent with respect to the $T < \theta$ conditions of PVCz and P1 in this solvent.

Unperturbed Dimensions. As is well-known, unperturbed dimensions can be evaluated from measurements of dimensions of the polymers as a function of molecular weight in a good solvent, using several extrapolation procedures. Usually these extrapolations are performed with monodisperse or nearly monodisperse samples obtained through fractionation procedures of a polydisperse polymer or using several monodisperse polymers obtained through anionic polymerization. When the SEC-MALS technique is applied to a broad polydisperse polymers, as in this case, there are a set of values of *M* and $\langle s^2\rangle$ (see Figure 7) that can be used to evaluate unperturbed dimensions.[5]

The Fixman[42] extrapolation was used in the present work. The procedure is defined in eq 15 and provides $\langle s^2\rangle_0/M$ as the intercept:

$$\frac{\langle s^2\rangle}{M} = \frac{\langle s^2\rangle_0}{M} + 0.0299B\left(\frac{\langle s^2\rangle_0}{M}\right)^{-1/2} M^{1/2} \tag{15}$$

The Fixman plot for PVCz in THF is represented by solid squares in Figure 9. The corresponding plot for copolymer P1 is similar, and it has not been depicted. The values of $\langle s^2\rangle_0/M$, in nm^2 mol g^{-1}, obtained from the Fixman extrapolations for both polymers are presented in Table 3. The characteristic ratio C_n can be calculated from the extrapolated values of $\langle s^2\rangle_0/M$ as[43]

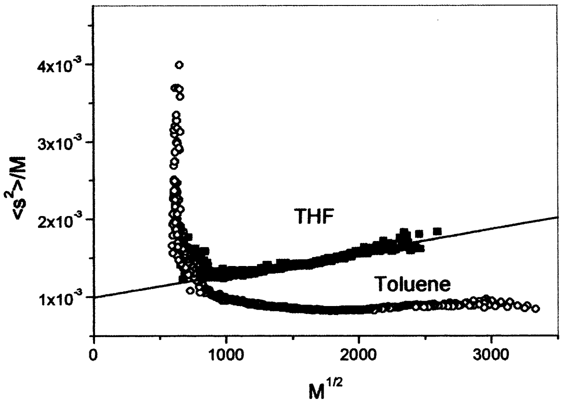

Figure 9. Unperturbed dimensions for PVCz in THF (■) and toluene (□).

$$C_n = \frac{\langle r^2\rangle_0}{nl^2} = \frac{6M_0}{2l^2}\frac{\langle s^2\rangle_0}{M} \tag{16}$$

where *n* is the number of bonds, each one of them having a length $l = 0.154$ nm in the present work, $\langle r^2\rangle_0$ the unperturbed value of the mean-square end-to-end distance, and M_0 the molecular weight of the repeating unit. The $\langle r^2\rangle_0 = 6\langle s^2\rangle_0$ relationship valid for flexible chains was used in the above equation. The values of C_n obtained (Table 3) are in very good agreement with the values reported in the literature for PVCz.[21,22,44]

Further evidence about the shrinkage of the PVCz chains in toluene can be obtained by examining the dependence of the chain expansion factor on molecular weight. The perturbed and unperturbed mean-square radius of gyration are related through the chain expansion factor, α:

$$\alpha^2 = \frac{\langle s^2\rangle}{\langle s^2\rangle_0} \tag{17}$$

and according to the two-parameter theory[45]

$$\alpha^2 = (1 + 1.276z - 2.082z^2 + ...) \tag{18}$$

where *z* is a parameter proportional to $M^{1/2}$ and to the excluded-volume interaction energy of the polymer system, which is negative if the system is under θ conditions.[46]

From the above equations, it follows that the values of $\langle s^2\rangle/M$ vs $M^{1/2}$ should fit the relationship

$$\frac{\langle s^2\rangle}{M} = \frac{\langle s^2\rangle_0}{M}(1 + AM^{1/2} + BM + ...) \tag{19}$$

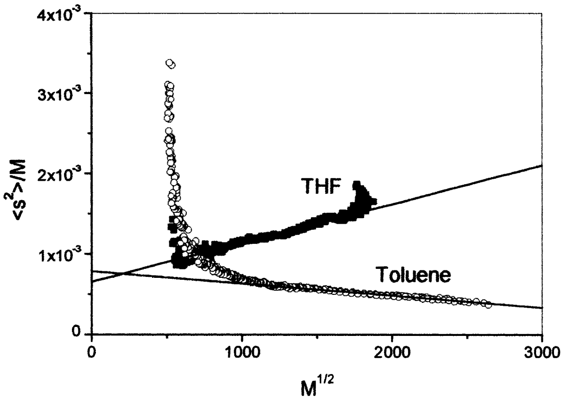

Figure 10. Unperturbed dimensions for copolymer P7 in THF (■) and toluene (□).

and with the omission of the z^2 and higher terms the relationship is linear, with a negative slope and $\langle s^2\rangle_0/M$ as the independent term. Hollow circles in Figure 9 show the experimental values of $\langle s^2\rangle/M$ vs $M^{1/2}$ for PVCz in toluene. As explained above, there is a curvature in the scaling law at low molecular weights. Thus, only the experimental points taken into account for the scaling law (Figure 7) are plotted in Figure 9. The negative slope exhibited by the extrapolation is a straight consequence of the under θ conditions of the system. Thus, the value of α should decrease below unity, and the ratio $\langle s^2\rangle/M$ will increase with decreasing M. The value of the intercept $(7.7 \pm 0.1) \times 10^{-4}$ nm^2 mol g^{-1} is close to, although somewhat higher than, that obtained by the Fixman extrapolation.

The three copolymers with higher MMA content also have similar unperturbed dimension extrapolation plots. The Fixman plot (eq 15) for P7 in THF is shown in Figure 10, and the unperturbed dimensions obtained for the three copolymers are presented in Table 3. In is interesting to notice the similarity in the behavior of these copolymers although their carbazole content is very different. The number-average length of the sequence of MMA units,[19] $\langle n_{\mathrm{MMA}}\rangle$, is presented in Table 3. As can be seen for copolymer P9, one carbazole group for every 23 MMA units is enough to expand the chain comparing with poly(methyl methacrylate)[5] whose C_n is 8.8.

At unperturbed conditions, $\langle s^2\rangle_0$ scales with M and therefore, the ratio $\langle s^2\rangle_0/M$ should be constant. Toluene is, according to the values close to 0.5 of the q parameter of the scaling law, a θ solvent for the three copolymers. The values of $\langle s^2\rangle/M$ for copolymer P7 in toluene are depicted, as hollow circles, in Figure 10 and are practically independent of M in the range of high molecular weights.

Theoretical calculation of the unperturbed dimensions. The unperturbed dimensions of the studied polymers were also theoretically calculated employing the rotational isomeric scheme[43,47,48] and standard procedures of the matrix multiplication scheme.[43,47–51] Only two orientations, namely trans ($\phi = 0°$) and gauche ($\phi = 120°$), were allowed to the rotations over the skeletal bonds since both Cz and MMA groups are very bulky and produce severe steric repulsions in any conformation containing negative gauche ($\phi = 240°$) orientations.[50,51]

Figure 11 shows a rough sketch of a segment of a Cz–MMA copolymer illustrating the five different kind of pairs of skeletal bonds that have to be considered in this chain. In the first place, bonds meeting at a substituted C, such as i, $i + 1$, $i + 2$, $i + 3$, etc., can be represented by a very simple statistical weight matrix:[43,47–50]

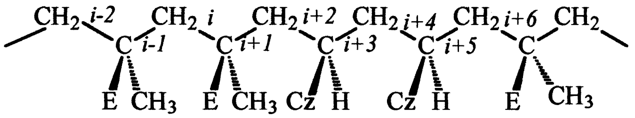

Figure 11. A segment of a *N*-vinylcarbazole–methyl methacrylate copolymer shown in its planar all-trans conformation that was taken as origin for rotations over the skeletal bonds (i.e., $\phi = 0$ for the conformation shown in this figure). E and Cz represent respectively methyl ester and carbazole groups.

$$U' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \tag{20}$$

where the rotational isomers are indexed in the order trans, gauche.

The two configurations (i.e., meso and racemic) for the pairs of bonds pertaining to a Cz–Cz dyad, such as bonds $i + 3$ and $i + 4$ in Figure 11, can be represented by the matrices:[50]

$$U_{\mathrm{m}}(\mathrm{Cz{-}Cz}) = \begin{bmatrix} {\eta_1}^2{\omega_1}'' & \eta_1 \\ \eta_1 & \omega_1 \end{bmatrix}$$

$$U_{\mathrm{r}}(\mathrm{Cz{-}Cz}) = \begin{bmatrix} {\eta_1}^2 & \eta_1\omega'_1 \\ \eta_1\omega'_1 & 1 \end{bmatrix} \tag{21}$$

where the subscript 1 indicates values for the Cz units (component 1). Statistical weights η, ω, ω', and ω'' were taken to be Boltzmann exponentials of their respective conformational energies, namely, first-order interactions for trans vs gauche states (η) and second-order interactions among CH_2...CH_2 (ω), CH_2...Cz (ω'), and Cz...Cz (ω'').

In the case of MMA units, the CH_3 side group is almost identical to the CH_2 group of the continuation of the chain and therefore produces ω and ω' interactions. Consequently, the statistical weight matrices for a MMA–MMA dyad, such as bond pair $i - 1$, i in Figure 11 may be written as[51,52]

$$U_{\mathrm{m}}(\mathrm{MMA{-}MMA}) = \begin{bmatrix} {\eta_2}^2\omega_2{\omega_2}'' & \eta_2\omega_2{\omega_2}' \\ \eta_2\omega_2{\omega_2}' & {\omega_2}^2 \end{bmatrix}$$

$$U_{\mathrm{r}}(\mathrm{MMA{-}MMA}) = \begin{bmatrix} {\eta_2}^2(\omega'_2)^2 & \eta_2\omega_2\omega'_2 \\ \eta_2\omega_2\omega'_2 & \omega^2 \end{bmatrix} \tag{22}$$

where the subscript 2 indicates values for MMA units.

The matrices for a Cz–MMA heterogeneous dyad, such as bond pairs $i + 5$, $i + 6$ in Figure 11, may be written as

$$U_{\mathrm{m}}(\mathrm{Cz{-}MMA}) = \begin{bmatrix} \eta_1\eta_2\gamma & \eta_2\omega'_1 \\ \eta_1\omega & \omega \end{bmatrix}$$

$$U_{\mathrm{r}}(\mathrm{Cz{-}MMA}) = \begin{bmatrix} \eta_1\eta_2\omega'_1 & \eta_1\omega'_1 \\ \eta_2\omega'_2 & \omega \end{bmatrix} \tag{23}$$

where γ represents the interaction among carbazole and methyl ester groups. No distinction has been made among the values of ω for either Cz or MMA units since in both cases it represents a CH_2...CH_2 interaction.

The last kind of dyad to be considered are the MMA–Cz, such as bond pair $i + 1$, $i + 2$ in Figure 11, and its

Table 4. Values of Conformational Energies, in kcal/mol, Employed for Cz and MMA Units

energy	Cz[a] (comp 1)	MMA[b] (comp 2)
E_η	−0.84	−1.8
E_ω	0.5	0.5
$E_{\omega'}$	0.5	0.5
$E_{\omega''}$	2.0	1.1

[a] Taken from ref 50. [b] Derived from ref 51.

statistical weight matrices can be obtained by interchanging tg and gt states in eq 23. Thus

$$U_{\mathrm{m}}(\mathrm{MMA{-}Cz}) = \begin{bmatrix} \eta_1\eta_2\gamma & \eta_1\omega \\ \eta_2\omega'_1 & \omega \end{bmatrix}$$

$$U_{\mathrm{r}}(\mathrm{MMA{-}Cz}) = \begin{bmatrix} \eta_1\eta_2\omega'_1 & \eta_2\omega'_2 \\ \eta_1\omega'_1 & \omega \end{bmatrix} \qquad (24)$$

Values of the conformational energies required to compute the statistical weights employed in eqs 21−24 are collected in Table 4 with the exception of E_γ, for which a value of 1.8 kcal/mol was employed.

Calculations were performed at 25 °C employing Monte Carlo procedures. Thus, chains containing 200 repeat units with the desired contents of Cz and PMMA units were generated. The meso fractions were set to $w_{\mathrm{m}}(\mathrm{Cz}) = 0.2$ and $w_{\mathrm{m}}(\mathrm{MMA}) = 0.4$ respectively for Cz and MMA units, which are the tacticities of these polymers when obtained by radical polymerization. The distribution of meso and racemic units along the chain was random in all the calculations. However, two different distributions of Cz and MMA units, namely block and random copolymers, were studied. One hundred independent configurations of each chain were generated, and for each configuration, 1000 different conformations were produced according to the a priori probabilities[43,47−49] extracted from eqs 19−24. Values of $\langle r^2\rangle_0$ for each conformation of the studied chain were computed (i.e., 10^5 values per chain), averaged, and transformed into characteristic ratio C_n. Standard error or the averages were smaller than 1%. The results obtained are shown in Figure 12 together with the experimental results.

Inspection of Figure 12 reveals that the unperturbed dimensions of block and random copolymers are quite different. The variation of C_n with the content of MMA units is roughly linear in the case of block distribution while the random distribution produces results that are much closer to those experimentally obtained. In fact, agreement between theory and experience is excellent in the case of both homopolymers and in copolymers with MMA content up to ca. 80%. However, in the case of very high content of MMA units, calculated values are ca. 20% smaller than the corresponding experimental results. A possible explanation for this discrepancy could be inhomogeneities in the chemical composition along the chain of copolymers with very high content of one monomer, i.e., too few units of the second monomer as to produce a good random distribution. Under these circumstances, both M and $\langle s^2\rangle$ might be overestimated, although the effect should be more important in $\langle s^2\rangle$ and therefore the experimental values of C_n could be overestimated. This fact would also explain the upward curvature observed in the molecular weight vs elution volume (Figure 5) at high elution volume observed in copolymer P9.

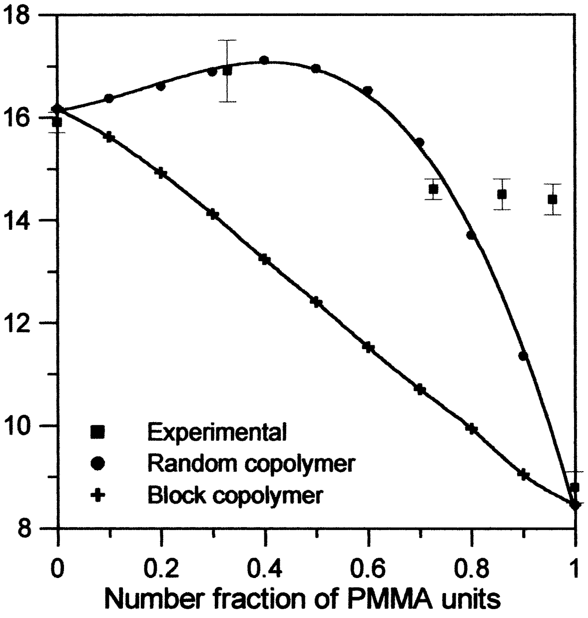

Figure 12. Variation of the characteristic ratio of the unperturbed dimensions, $C_n = \langle r^2\rangle_0/nl^2$, with the number fraction of carbazole units. Both measurements and calculations were performed at 25 °C.

Conclusions

Application of SEC techniques with multiple detectors can be used to study the solution properties of copolymers formed by CZ and MMA units. Experimental measurements performed at 25 °C, in both toluene and THF solutions, allows the evaluation of molecular weight averages and distributions, molecular dimensions, scaling law coefficients, etc. Calculations of the unperturbed dimensions performed with a very simple rotational isomeric states model and assuming random distribution of Cz and MMA units along the chain provide results which are in very good agreement with experimental values except in the case of copolymers with a very high content of MMA units.

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(52) The number of parameters in eq 22 may be reduced to just 2, namely α and β, through division of both matrices by $\eta^2\omega\omega''$ (i.e., the 11 element of U_m) and definition of $\alpha = \omega'/\eta\omega''$ and $\beta = \omega'^2/\omega\omega''$. The α and β parameters are employed in ref 51; however, we have preferred to use the full set to conform with the scheme of PVCz and facilitate the formulation of the matrices for the heterogeneous dyads.

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