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Viscometric Study of Poly(2-cinnamoyloxyethyl methacrylate)

Liangzhi Hong and Guojun Liu*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6

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ABSTRACT: Six poly(2-cinnamoyloxyethyl methacrylate) (PCEMA) samples with low polydispersity indices were derived from precursors prepared by anionic polymerization. Their intrinsic viscosities were determined in tetrahydrofuran (THF) and chloroform at 25 °C and in *p*-xylene between 55 and 82 °C. The data were treated to yield the Mark−Houwink−Sakurada parameters *K* and *a*. The *a* values suggested that THF and chloroform were good solvents for PCEMA at room temperature. The intrinsic viscosity data obtained in *p*-xylene were also analyzed by the Burchard−Stockmayer−Fixman method. Both the *a* values and the results of data treatment by the Burchard−Stockmayer−Fixman method suggest that *p*-xylene was a theta solvent for PCEMA at 60 °C. Using the *K* value at the theta temperature, we determined for PCEMA a characteristic ratio of 12.6, which is the ratio between its mean-square end-to-end distance in a theta solvent and that of a random flight chain.

I. Introduction

Poly(2-cinnamoyloxyethyl methacrylate) (PCEMA, Scheme 1) is an interesting polymer. Upon irradiation with light at ~274 nm, two CEMA units can readily undergo 1,4-dimerization, and the dimerization of CEMA units from different polymer chains results in polymer photo-cross-linking.[1,2] The photo-cross-linking of block copolymers containing CEMA units allows the efficient locking of structures of block copolymer assemblies. We have taken advantage of this chemistry to prepare "permanent" block copolymer nanostructures, including star polymers,[1,3] nanospheres,[1,4−7] nanofibers,[3,8,9] and cross-linked vesicles.[10] Further chemical processing, such as selective domain degradation, of these "permanent" block copolymer nanostructures has allowed us to prepare "permanently sculpted" nanostructures, including nanotubes[11−14] and thin films containing nanochannels.[15−17] More recently, we have used PCEMA photo-cross-linking chemistry to lock in preassembled molecular assemblies to yield permanent molecular architectures, including tadpole molecules[18,19] and macrocycles.[20] Aside from using this method for architectural preparation, it has been used to facilitate the elucidation of structures of complex ABC triblock copolymer micelles. After the photo-cross-linking of the PCEMA domains in a micelle, other blocks in the structurally stable micelles could be derivatized to facilitate their selective staining for identification by electron microscopy.[21,22] Most interestingly, micelles with PCEMA cores in automobile engine base oils were discovered to possess unique friction reduction abilities.[23]

Despite the extensive use of PCEMA by our group in various projects and its fascinating friction-reduction properties, and despite its use by other groups,[24−33] little is known about its solution properties. For example, it was not known which solvents behaved as theta solvents for this polymer. The characteristic ratio (C_∞) of this polymer, which is the ratio between its mean-square end-to-end distance in a theta solvent and that for a random flight chain, was unknown. This C_∞ value is important because we frequently need to know if the PCEMA chains of a self-assembled block copolymer structure are stretched relative to their unperturbed state. This study was initiated mainly to address these issues.

Six PCEMA samples with low polydispersity were derived from precursors prepared by anionic polymerization. Their intrinsic viscosities were determined in tetrahydrofuran (THF) and chloroform at 25 °C and in *p*-xylene at temperatures between 50 and 82 °C. This data was used to evaluate the Mark−Houwink−Sakurada parameters *K* and *a*, and for the determination of the theta temperature of PCEMA in *p*-xylene. The data was used also for the determination of C_∞ for PCEMA.

II. Experimental Section

Materials. THF (Fisher Scientific, 99.9+%) was distilled over sodium metal in the presence of benzophenone before use. Chloroform (Fisher Scientific, 99.8+%) and *p*-xylene (Sigma-Aldrich, anhydrous, 99+%) were used as received.

Six PCEMA samples, P1−P6, with molecular weights increasing from P1 to P6, were used in this study. The polymers were derived from the reaction of cinnamoyl chloride (Aldrich, 98%) with poly(2-hydroxyethyl methacrylate) (PHEMA). PHEMA was obtained from the hydrolysis of poly(2-trimethylsiloxyethyl methacrylate), or P(HEMA-TMS). The P(HEMA-TMS) samples were prepared from the anionic polymerization of HEMA-TMS. 1,2-Diphenyl-3-methylpentyllithium, generated in situ from reacting *sec*-butyl lithium with 1,1-diphenylethylene was used as the initiator. The polymerizations were performed in THF at −78 °C, and were terminated with degassed methanol. Because these preparations were standard and had been reported previously by our group,[34,35] the detailed procedures are not repeated here.

Polymer Characterization. The polymers were characterized by an Agilent size exclusion chromatograph (SEC) equipped with a Wyatt Optilab rEX refractive index detector and a Wyatt Dawn Heleos II light scattering detector. The eluant used was THF, and the columns used were of MZ-Gel SD Plus with nominal pore sizes of 500, 10^4, and 10^5 Å, respectively. The differences among the refractive indices (Δn_r) of P2, P3, and P6 solutions in THF at different concentrations (*c*) and that of THF were determined at 25.0 °C, using the Optilab rEX detector in batch mode. The specific refractive index increments (dn_r/dc) were obtained from the slope of the plot of Δn_r increases with *c*.

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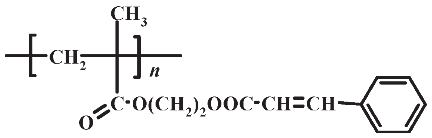
*Corresponding author.

Scheme 1. Structure for PCEMA



Both the Heleos II light scattering detector and the Optilab rEX refractive index detector used light sources with an emission wavelength of 660 ± 10 nm.

^1H and ^{13}C NMR analyses of the samples were recorded in $CDCl_3$ at 25.0 °C on a Bruker Avance-500 (DRX) NMR spectrometer. The nuclear Overhauser enhancement (NOE) effect in ^{13}C spectra was suppressed by inverse gated decoupling.[36,37]

Viscosity Measurements. Flow times of PCEMA solutions in THF, chloroform, and *p*-xylene and those of the solvents were measured using a Ubbelohde capillary viscometer. Relative viscosity (η_r) was obtained from the ratio of the flow times of a solution and the solvent. Before each measurement, a solution in the viscometer was sealed and allowed to equilibrate with a thermostatted water tank for at least 0.5 h. The temperature fluctuation of the water tank was < 0.05 °C. All samples used for flow time measurements were clarified by filtration through Whatman 0.2 μm Teflon filters. At least five flow times were recorded for each sample. The relative error in the flow times was < 0.1%.

The η_r values were determined at several concentrations c for each PCEMA sample in THF and chloroform. The η_r data were analyzed using the Huggins equation to yield the intrinsic viscosity $[\eta]$ and the Huggins constant k_h[38]

$$(\eta_r - 1)/c = [\eta] + k_h[\eta]^2 c \tag{1}$$

The intrinsic viscosities of PCEMA in *p*-xylene at different temperatures were determined from the single-concentration method using the Solomon and Ciuta equation[39]

$$[\eta] = \sqrt{2((\eta_r - 1) - \ln \eta_r)}/c \tag{2}$$

In these measurements, low polymer concentrations were used so that $\eta_r < 1.1$. The use of low c values was important because eq 2 was derived from the Huggins equation by neglecting the higher-order c terms.

The molar volume $V_m(T)$ of *p*-xylene at different temperatures was calculated using the Rackett equation[40]

$$V_m(T) = A_2 \times A_1^{[1 + (1 - T/T_c)^{2/7}]} \tag{3}$$

where $A_2 = 1.4655 \times 10^{-3}$ m^3/mol, $A_1 = 0.25888$, and $T_c = 616.26$ K. The calculated solvent volumes for a given sample were then used to calculate the correct polymer concentrations at different temperatures.

III. Results and Discussion

Polymer Characteristics. The specific refractive index increments dn_r/dc were determined for three of the six PCEMA samples P2, P3, and P6, and the results are shown in Table 1. These values were the same within experimental error. This observation was in accord with the empirical conclusion that the dn_r/dc values of homopolymers do not change significantly with polymer molecular weight once it is above ~10 000 Da.[41]

The polymers were characterized using an SEC system equipped with both a refractive index and a light scattering detector. Using the experimentally determined dn_r/dc value, we were able to make an absolute determination of the molecular weights and polydispersity indices M_w/M_n of all of the samples. The results are shown in Table 1.

Table 1. Characteristics of the PCEMA Homopolymers Used

sample	dn_r/dc (mL/g)	M_w/M_n	10^{-4} M_w (g/mol)	n_w
P1	[a]	1.02	4.1	160
P2	0.163	1.02	5.0	190
P3	0.162	1.02	8.4	320
P4	[a]	1.01	8.5	330
P5	[a]	1.03	17.0	650
P6	0.163	1.02	28.8	1180

[a] Not determined.

The M_w/M_n values were all low. This should not be surprising because the polymers were derived from precursors prepared by anionic polymerization. From the determined weight-average molecular weights (M_w), the weight-average numbers (n_w) of repeat units were 160, 190, 320, 330, 650, and 1180, for P1 through to P6, respectively. P1, with an n_w value close to that of P2, and also P4, with its n_w close to that of P3 were prepared because we ran out of samples P2 and P3 in the later stages of this project.

The tacticity of P5 was determined by ^{13}C NMR.[37,42] Comparing the integrated areas of the peaks of the PCEMA quaternary backbone carbon atoms belonging to different triads, we determined that the fraction of atoms belonging to syndiotactic triads (*rr*) was 80.3%, that belonging to heterotactic triads (*mr*) was 19.5%, and that belonging to isotactic triads (*mm*) was 0.2%. Therefore, the polymer was essentially syndiotactic. This should be true for the other PCEMA samples as well. The production of syndiotactic PCEMA should not be surprising because most polymethacrylates prepared from anionic polymerization at −78 °C are syndiotactic.[37]

We have also synthesized a PCEMA sample with 3800 repeat units. However, its polydispersity was 1.6. Therefore, this sample was not used for further study. Well-defined samples with high molecular weights were difficult to prepare because of the small amounts of initiator used and thus the reduced tolerance for impurities.

Intrinsic Viscosity Data. Relative viscosities, η_r, were determined for the PCEMA samples at different concentrations in THF and chloroform. In Figure 1 are plotted $(\eta_r - 1)/c$ versus c for the samples in the two solvents. From the straight lines and following eq 1, we obtained the intrinsic viscosity $[\eta]$ of each sample as the intercept. The Huggins parameter, k_h, was obtained from the combined use of the slope and the intercept values. These values are listed in Table 2.

The intrinsic viscosities $[\eta]$ of the samples in *p*-xylene at different temperatures were determined using the single-concentration method. These values are plotted as a function of temperature in Figure 2.

The single-point method was used here because it is accurate enough for the measurement of viscosities of polymer solutions near the theta state. The single-point method is most accurate when $k_h = 1/3$.[43−45] According to Yamakawa[46]

$$k_h = \frac{1}{2}\left[1 - 3\left(\frac{A_2 M}{[\eta]}\right)\varphi\right] \tag{4}$$

where A_2 is the second virial coefficient, M is molar mass of the polymer, and φ is a complex function of the excluded volume parameter. In a theta solvent, A_2 is zero and k_h is 0.50. At this k_h value, the value of $[\eta]$ determined from the single-concentration method should be larger than that determined from the concentration extrapolation method by < 2% if $\eta_r < 1.10$.[43]

We did not use the single-concentration method for the determination of $[\eta]$ of the PCEMA samples in good solvents, THF and chloroform, because the k_h value would

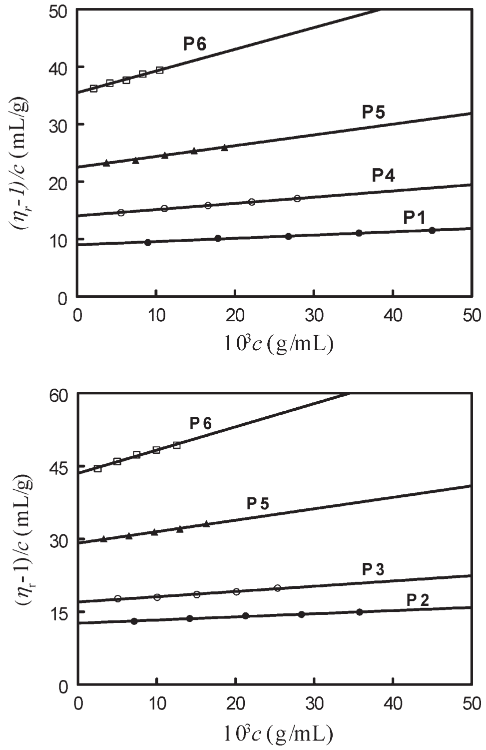


Figure 1. Plots of $(\eta_r - 1)/c$ versus c for PCEMA solutions in THF (top frame) and in chloroform (bottom frame).

Table 2. Intrinsic Viscosities and Huggins Parameters of PCEMA Determined in Different Solvents and at Different Temperatures

sample	k_h	$[\eta]$ (mL/g)
	THF at 25.0 ± 0.1 °C	
P1	0.69	9.0
P4	0.55	14.0
P5	0.37	22.5
P6	0.30	35.5
	Chloroform at 25.0 ± 0.1 °C	
P2	0.41	12.6
P3	0.38	17.0
P5	0.28	29.1
P6	0.25	43.5

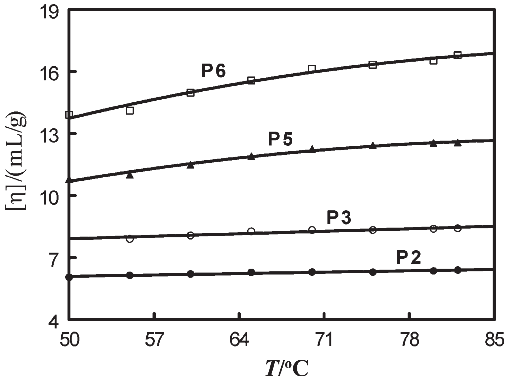


Figure 2. Plots of intrinsic viscosity $[\eta]$ change with temperature, T, for PCEMA samples P2 (●), P3 (○), P5 (▲), and P6 (□) in p-xylene.

change significantly with M. This variation of k_h with M is clearly seen in Table 2.

Comparing the $[\eta]$ values of Table 2 and Figure 2, we notice the following trends. First, the $[\eta]$ values of a given polymer sample decreased as the solvent was changed from chloroform to THF and then to p-xylene. Whereas the $[\eta]$ values were comparable in chloroform and THF, the values were substantially lower in p-xylene. Second, the $[\eta]$ values showed more pronounced increases for the higher-molecular-weight PCEMA samples as T increased.

Theoretically, the intrinsic viscosity is given by[47]

$$[\eta] = \Phi_0 \langle R_n{}^2 \rangle^{3/2}/M \tag{5}$$

where Φ_0, the Flory hydrodynamic constant, is 2.5×10^{23}/mol if the units of $[\eta]$ are in milliliters per gram, $\langle R_n{}^2 \rangle$ is the mean-square end-to-end distance of polymer chains, and M is the molar mass of the polymer. Evidently, $[\eta]$ is inversely proportional to the density of polymer coils in a given solvent.

A higher $[\eta]$ in chloroform than in THF at 25 °C suggests that the PCEMA chains had expanded more in chloroform than in THF. Therefore, chloroform should be a better solvent for PCEMA than THF. The $[\eta]$ values are substantially lower in p-xylene than in THF and chloroform because p-xylene was close to a theta solvent for PCEMA.

At a given temperature, the Mark−Houwink−Sakurada (MHS) equation holds for samples of different molecular weights if the sample molecular weights are sufficiently high[48]

$$[\eta] = KM^a \tag{6}$$

The intrinsic viscosity ratio at different temperatures for a given sample is

$$[\eta]_2/[\eta]_1 = (K_2/K_1)M^{a_2 - a_1} \tag{7}$$

For a positive $a_2 - a_1$, $[\eta]_2/[\eta]_1$ increases with increasing molecular weight, M. This explains why $[\eta]$ increased more steeply with T as PCEMA molecular weight increased.

We notice in Table 2 that the Huggins constant k_h for a given sample in THF was always larger than that in chloroform. For linear nonpolar flexible chains, k_h is normally between 0.30 and 0.60.[48] The Huggins constant, k_h, is a measure of the relative strength of segment−segment and segment−solvent interactions. For polymer−solvent binary systems, a less favorable polymer−solvent contact leads to a higher k_h value.[49,50] This is in agreement with our prior conclusion that THF was not as good a solvent as chloroform for PCEMA.

Mark−Houwink−Sakurada Parameters. The $[\eta]$ values at a given temperature in a particular solvent should follow the MHS equation. We have thus plotted data in Table 2 and in Figure 2 in the form of $\ln[\eta]$ versus $\ln M_w$. Figure 3 shows the $\ln[\eta]$ versus $\ln M_w$ plots for the THF and chloroform samples at 25 °C and the p-xylene samples at 60 °C. From the slopes and intercepts of these plots, we obtained the K and a values.

Table 3 lists the K and a values that were generated from the $\ln[\eta]$ versus $\ln M_w$ plots. The MHS exponents a were 0.71 ± 0.03 and 0.70 ± 0.04 in chloroform and THF, respectively, at 25 °C. In p-xylene, a increased with T and reached a maximum value of 0.551 ± 0.005 at 82 °C.

The MHS exponent a provides a measure for the degree of polymer coil expansion in various solvents. For flexible polymer chains in a good solvent, the a value should be between 0.70 and 0.80.[51] Evidently, chloroform is a better solvent for PCEMA than THF. The fact that $a = 0.501 \pm 0.001$ at 60.0 °C suggests that p-xylene was essentially a theta solvent for PCEMA at this temperature. As the temperature increased, the solvent quality improved and a increased.

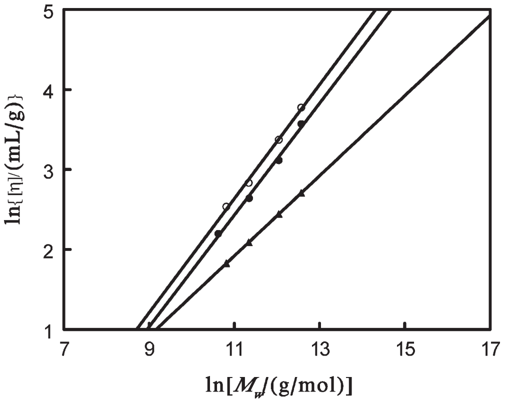


Figure 3. Plots of $\ln[\eta]$ versus $\ln M_w$ for the PCEMA samples in THF (●) and chloroform (○) at 25 °C and *p*-xylene (▲) at 60 °C.

Table 3. Mark−Houwink−Sakurada Parameters for PCEMA in Different Solvents at Different Temperatures

solvent	temperature/°C	K ($\times 10^3$)/(mL/g)	a
chloroform	25.0	5.5 ± 1.7	0.71 ± 0.03
THF	25.0	5.2 ± 2.3	0.70 ± 0.04
p-xylene	82.0	16.4 ± 0.5	0.551 ± 0.005
p-xylene	80.0	17.1 ± 0.6	0.547 ± 0.006
p-xylene	75.0	17.3 ± 0.6	0.545 ± 0.006
p-xylene	70.0	19.1 ± 0.3	0.536 ± 0.003
p-xylene	65.0	23.9 ± 0.2	0.516 ± 0.002
p-xylene	60.0	27.6 ± 0.1	0.501 ± 0.001
p-xylene	55.0	37.2 ± 0.4	0.473 ± 0.003

Whereas the error margins for the K and a values determined in *p*-xylene were small, they were much larger for the K values determined in THF and chloroform. We initially suspected that this was due to errors in $[\eta]$ determination. We repeated the $[\eta]$ determination in THF, and similar results were obtained. Therefore, the uncertainty in K must be due to the use of good, rather than theta, solvents in this case. Our literature search revealed that the MHS equation holds only for high molar mass polymers in good solvents when the excluded volume effect is present. As the molecular weight decreases, the excluded volume effect vanishes progressively to zero, and the contribution of local chain conformation increases.[52−54] This gradual appearance of the excluded volume effect with increasing molecular weight is absent in a theta solvent. Therefore, the large uncertainties in K in the good solvents were a direct consequence of the use of samples with insufficiently high molecular weights. We could not have refined our study further because we could not prepare well-defined samples with higher molecular weights.

Theta Temperature. The Burchard−Stockmayer−Fixman (BSF) method is normally used for the precise determination of the theta temperature (T_θ) of a polymer.[55−57] This method invokes first the plotting of the $[\eta]$ data of a series of samples at each of several temperatures in the form of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$. In the neighborhood of T_θ, the relationship can be expressed as

$$[\eta]/M_w^{1/2} = K_\theta + c(T)M^{1/2} \tag{8}$$

where K_θ is the MHS K parameter at T_θ. According to the ellipsoid polymer model,[58−60] the slope $c(T)$ is

$$c(T) = 0.51\Phi_0 B_0(1 - T_\theta/T) \tag{9}$$

where B_0 is a constant independent of temperature.[57] Therefore, plotting $c(T)$ versus $1/T$ allows one to interpolate T_θ at the point $c(T) = 0$.

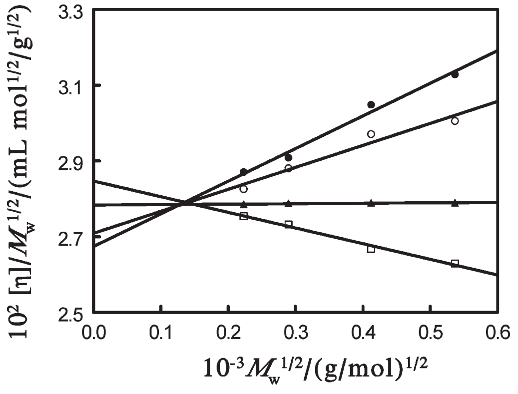


Figure 4. Plots of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ for PCEMA samples in *p*-xylene at 82 (●), 70 (○), 60 (▲), and 55 °C (□).

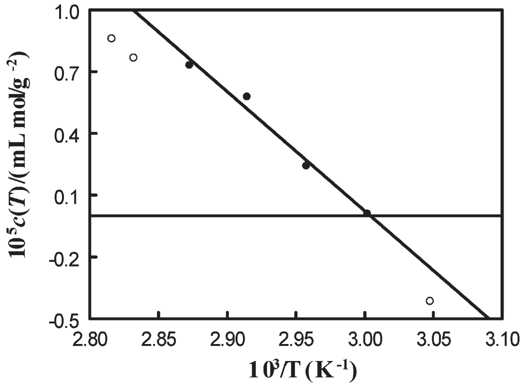


Figure 5. Plot of $c(T)$ versus $1/T$ for PCEMA data obtained in *p*-xylene.

Figure 4 shows $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ plots for PCEMA at 82, 70, 60, and 55 °C. Analogous plots were obtained at 80, 75, and 65 °C. We note that the slope, c, changed from positive to negative as T was decreased from 82 to 55 °C. According to eq 8, T_θ must occur between these two temperatures.

Figure 5 shows plots $c(T)$ versus $1/T$ for PCEMA data obtained in *p*-xylene. The data close to T_θ were used to extrapolate the T_θ value using eq 8. This temperature was found to be 60.0 °C, which agreed with the MHS exponent of 0.501 for PCEMA measured at 60 °C.

The deviation of the data at higher temperatures from the straight line in Figure 5 was expected because the BSF equation holds only in the vicinity of the theta temperature.[56,57] As T increases and the polymer coils expand more, the draining effect sets in, and eq 8 becomes invalid.

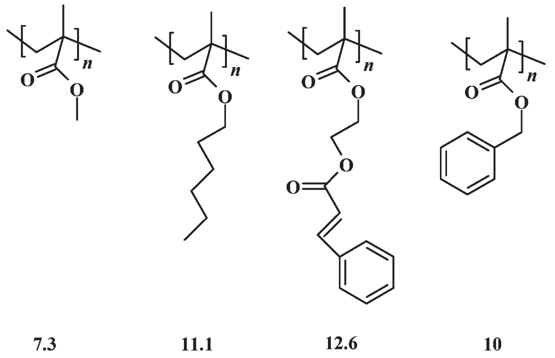
Unperturbed Dimension. For coils that are close to their theta conformations or are not overly expanded, eq 7 is very useful for extrapolating the K_θ value. Treating the $[\eta]$ data obtained in *p*-xylene at temperatures between 55 and 82 °C using eq 7, we obtained an average K_θ value of $(2.74 \pm 0.08) \times 10^{-2}$ mL/g. This agreed well with the K_θ value of 2.76×10^{-2} mL/g obtained from treating the $[\eta]$ data in *p*-xylene at 60 °C by the MHS equation.

According to Flory and Fox[47]

$$K_\theta = \Phi_0 \left[\frac{\langle R_{n0}^2\rangle}{M}\right]^{3/2} \tag{10}$$

where $\langle R_{n0}^2\rangle$ is the unperturbed mean-square end-to-end distance at the theta state. Using $K_\theta = 2.76 \times 10^{-2}$ mL/g and $\Phi_0 = 2.5 \times 10^{23}$ mol^{-1}, we obtained $\langle R_{n0}^2\rangle / M_w = 2.30 \times 10^{-3}$ nm^2

Scheme 2. Comparison of the Structures and C_∞ Values of Several Polymethacrylates



mol/g. Replacing M_w with n_w and inserting the bond length, l, of 0.154 nm for C−C bonds in the above relation, we can also rewrite $\langle R_{n0}^2\rangle$ as

$$\langle R_{n0}^2\rangle = 12.6(2n_w l^2) \quad (11)$$

where $2n_w$ denotes the weight-average number of bonds per chain. Therefore, the characteristic ratio C_∞ of PCEMA is 12.6.

Much effort has been made to correlate C_∞ with the structure of polymer repeat units.[58] For polymethacrylates alone, C_∞ values have been determined for more than 50 polymers of this family.[61] Compared below are the C_∞ values and structures of several polymethacrylates[58] (Scheme 2) and those of PCEMA.

From poly(methyl methacrylate) to poly(hexyl methacrylate), C_∞ increased because of the size increase in the alkyl group. A cinnamoyloxyethyl group is evidently larger than a hexyl group. Therefore, a further increase in C_∞ from poly(hexyl methacrylate) to PCEMA was reasonable. The C_∞ value of PCEMA was larger than that for poly(benzyl methacrylate), again because of the larger size of the cinnamoyloxyethyl group compared with the benzyl group.

IV. Conclusions

Six PCEMA homopolymers were synthesized and characterized. Their intrinsic viscosities were determined in THF and chloroform at 25.0 ± 0.1 °C and in *p*-xylene between 50 and 82 °C. The data were used to evaluate the Mark−Houwink−Sakurada parameters. The exponents suggest that THF and chloroform were good solvents for PCEMA and *p*-xylene was a theta solvent for PCEMA at 60 °C. The theta condition was confirmed by treating the intrinsic viscosity data using the Burchard−Stockmayer−Fixman method. From the MHS parameter, K_θ, determined at the theta temperature, we calculated a characteristic ratio of 12.6 for PCEMA. This value was reasonable when compared with those of other polymethacrylates with pendant groups of varying bulkiness.

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