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Solution Properties and Chain Dimensions of Poly(*n*-alkyl methacrylates)

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ABSTRACT: The influence of *n*-alkyl side-chain length on the unperturbed chain dimensions of poly(*n*-alkyl methacrylates) has been examined. For the cases where the side-chain groups were decyl (C_{10}), tridecyl (C_{13}), stearyl (C_{18}), and docosyl (C_{22}), the unperturbed dimensions expressed in terms of the characteristic ratio were found to be, respectively, 13.0, 14.7, 20.4, and 23.6. This trend demonstrates that a change in the identity of the *n*-alkyl group is reflected in the unperturbed posture of the chain backbone.

Introduction

The influence of side groups on the unperturbed dimensions of substituted polyethylene chains is well documented.[2] In the case of the polymethacrylates, interest has focused on the changes induced by altering the length of the *n*-alkyl ester group (methyl to dodecyl)[3-8] or the identity of the ester linkage, e.g., as in poly(cyclohexyl methacrylate) and poly(*S*-cyclohexyl thiomethacrylate).[9,10]

An understanding of the properties of such poly(*n*-alkyl methacrylates) is at least particularly dependent on the ability to relate their equilibrium configuration-dependent behavior to their structure. The application of matrix methods[11,12] in the form of the rotational isomeric state (RIS) model has been used to calculate configurational properties, e.g., Flory's characteristic ratio (C_∞), for various polymers. The general approach involves a consideration of bond lengths and angles as well as the short-range contributions to potentials affecting rotation about the main-chain bonds.

The RIS model, though, has not been used to evaluate the influence of the chain length of the *n*-alkyl ester group on the unperturbed chain dimensions of the poly(*n*-alkyl methacrylates). This paper presents our experimental findings pertaining to C_∞ for poly(*n*-alkyl methacrylates) where the *n*-alkyl group was decyl (PDMA), tridecyl (PTDMA), stearyl (PSMA), or docosyl (PDCMA).

Experimental Section

The decyl, tridecyl, and stearyl methacrylate monomers were obtained from Polysciences, Inc. The docosyl methacrylate monomer was synthesized in toluene as follows:

$$CH_2{=}C(CH_3){-}CO{-}OCH_3 + n\text{-}C_{22}H_{45}OH \rightarrow CH_2{=}C(CH_3){-}CO{-}OC_{22}H_{45} + CH_3OH$$

with *p*-toluenesulfonic acid as the catalyst. The methanol was distilled off during the reaction. The solid docosyl methacrylate was then purified by recrystallization from hexane solution at ca. −30 °C. The monomer was then vacuum-dried. Both ^1H NMR and IR were used to check monomer purity. The results indicated that all the monomers used in this work were virtually free of impurities.

Table I
Refractive Index Differences for Poly(*n*-alkyl methacrylates)

sample	solvent	temp, °C	d*n*/d*c*
PDMA	cyclohexane	30	0.0544[a]
	ethyl acetate	25	0.1146[b]
PTDMA	tetrahydrofuran	30	0.0828[a]
	ethyl acetate	27	0.1209[b]
PSMA	cyclohexane	20	0.0539[a]
	n-propyl acetate	36	0.1070[b]
PDCMA	cyclohexane	30	0.0545[a]
	amyl acetate	31	0.0903[b]

[a] 633 nm. [b] 436 nm.

The solution polymerizations were done under vacuum at 50 °C using purified AIBN as the initiator and benzene as the solvent. Two polymerizations were done for each monomer. The samples were fractionated using dilute (~1% (w/v)) toluene solutions with methanol as the nonsolvent. All of the solvents used in this work were dried and distilled prior to use. GC analysis of these solvents did not reveal any impurities.

Polymer molecular weight characterization was done using a combination of light scattering, membrane osmometry, and size exclusion chromatography (SEC). The Chromatix KMX-6 low-angle laser photometer (λ = 633 nm) was used for the light scattering molecular weight measurements while the Sofica PGD (λ = 436 nm) was used for the Θ temperature determinations. The d*n*/d*c* values were determined with the Chromatix KMX-16 refractometer (λ = 633 nm) and the Brice-Phoenix refractometer (λ = 436 nm). These results are shown in Table I.

The respective Θ temperatures were determined in the usual fashion by plotting the light scattering second virial coefficient

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Table II
Microtacticity of Poly(*n*-alkyl methacrylates)

polymer	rr	mr + rm	mm
PDMA	69	29	2
PTDMA	70	28	2
PSMA	70	28	2
PDCMA	63	33	4

(A_2) as a function of temperature. The Θ temperature was then taken as that temperature at which $A_2 = 0$. The d*n*/d*c* values were corrected as follows:

$$\mathrm{d}(\mathrm{d}n/\mathrm{d}c)/\mathrm{d}T \simeq 10^{-3}$$

for increasing temperature. This was done in order to determine the corresponding A_2 values from the slopes of c/I_{90} against concentration (c).

The osmometric molecular weights were measured with a Hewlett-Packard 503 instrument equipped with an S and S-08 membrane. Toluene was the measurement solvent at a temperature of 37 °C. The Ana-Prep instrument had a seven-column Styragel set with a porosity range 10^6–10^3 Å. Tetrahydrofuran was the carrier solvent. The characteristics of this column arrangement have been given elsewhere.[13,14]

The dilute solution viscosities were measured in semimicro Cannon-Ubbelohde viscometers where the solvent flow times were at least 110 s. The flow times were determined with the use of the Wescan 221 automatic timing device. The intrinsic viscosity values were determined by the usual extrapolation to zero concentration of the η_{sp}/c vs. c data.

The polydispersity ($\bar{M}_w/\bar{M}_n$) of the various fractions was estimated by size exclusion chromatography. The polydispersity indices were determined by Benoit's method[15] where the Mark–Houwink–Sakurada relation used for polystyrene[16] was $[\eta] = 1.02 \times 10^{-4} M_w^{0.73}$. The intrinsic viscosity relations used for the poly(*n*-alkyl methacrylates) were those developed in this work. The SEC polydispersity values, corrected for diffusion spreading,[17] agreed well with those values determined by light scattering and osmometry. The peak position of the chromatograms is recorded in terms of counts where the interval between counts is equal to 5 mL.

The microtacticity of the poly(*n*-alkyl methacrylates) was determined[18] from the ^{13}C NMR spectra obtained using *o*-dichlorobenzene (ca. 20% (w/w)) at 120 °C. The populations of the syndiotactic (rr), heterotactic (mr + rm), and isotactic (mm) triads are given in Table II.

Results and Discussion

The unperturbed dimensions of a linear, flexible macromolecule are obtainable by either light scattering over an angular range or dilute solution viscometry on polymers in ideal solvents (Θ conditions). For data obtained from nonideal solvents, extrapolation procedures are available[19-25] which allow the determination of the unperturbed chain dimensions. Our approach has been to rely upon results obtained from intrinsic viscosity measurements under Θ or near-Θ conditions. An alternative approach would involve the data obtained in the nonideal solvent tetrahydrofuran which can be evaluated by the procedure developed by Burchard[20] and Stockmayer and Fixman.[21]

The dilute solution characterization results are given in Tables III–VI for the four long-side-chain poly(*n*-alkyl methacrylates). Several observations can be made regarding some of the information contained in Tables III–VI. The relationships between the second virial coefficients and molecular weights, $\bar{M}_n$ or $\bar{M}_w$, yield exponents ranging from −0.41 to −0.23. These values are comparable to values found for other flexible polymers[10,26-29] but differ, in part, from the predicted limiting value[30] of −0.2. The values for the Huggins coefficients under Θ or near-Θ conditions and in good solvents generally follow the observed trends and theoretical predictions[31] for flexible polymers. These findings serve as semiquantitative indications that the poly(*n*-alkyl methacrylates) having relatively long side alkyl groups do not exhibit abnormal behavior in dilute solution; e.g., polymer aggregation via side group association does not occur over the concentration range (<1 wt %) examined.

Table III
Molecular Characteristics of Poly(decyl methacrylates) (PDMA)

sample	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$,[a] mol cm^3 g^{-2}	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$,[b] mol cm^3 g^{-2}	$[\eta]_{30^\circ\mathrm{C}}^{\mathrm{THF}}$, dL g^{-1}	k_H	$[\eta]$,[c] dL g^{-1}	k_H	SEC[d] V_e	$\bar{M}_w/\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[f]
II-1	65.4	1.9_9	92.3	1.9_1	1.04_8	0.31	0.32_0	0.78	43.3	1.41	1.39
II-2	47.0	2.3_4	62.5	2.3_5	0.76_8	0.32	0.27_2	0.69	44.8	1.33	1.29
II-3	29.4	2.7_8	38.9	2.7_8	0.52_9	0.36	0.20_9	0.69	46.6	1.32	1.24
I-1	20.1	3.1_1	30.2	2.3_8	0.46_7	0.33	0.18_8	0.93	47.6	1.50	1.40
II-4	16.7	2.6_5	21.1	2.7_3	0.35_5	0.33	0.16_0	0.88	48.8	1.26	1.20
I-2	11.9	3.5_2	16.2	2.9_8	0.31_3	0.43	0.14_6	0.91	49.5	1.36	1.30
II-5	9.2_0	4.3_1	12.5	3.6_3	0.23_4	0.44	0.12_2	0.88	50.9	1.36	1.30
I-3	7.8_6	4.0_3	10.3	3.4_4	0.21_3	0.44	0.11_3	1.35	51.5	1.31	1.22
I-4	4.5_4	5.8_1	6.2_2	3.2_0	0.14_6	0.44	0.08_7	1.07	53.8	1.37	1.13
I-5			2.9_3	6.6_4	0.081_4	0.97	0.06_1	1.22	56.5		1.35

[a] $A_2 = 2.7_2 \times 10^{-2} \bar{M}_n^{-0.37}$. [b] $A_2 = 1.0_3 \times 10^{-2} \bar{M}_w^{-0.29}$. [c] Θ conditions; ethyl acetate, 11 °C. [d] $\log \bar{M}_w = 10.87 - 0.1136 V_e$; $\log([\eta]\bar{M}_w) = 14.49 - 0.1967 V_e$; V_e denotes peak position. [e] Absolute molecular weight measurements. [f] SEC.

Table IV
Molecular Characteristics of Poly(tridecyl methacrylates) (PTDMA)

sample	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$,[a] mol cm^3 g^{-2}	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$,[b] mol cm^3 g^{-2}	$[\eta]_{30^\circ\mathrm{C}}^{\mathrm{THF}}$, dL g^{-1}	k_H	$[\eta]$,[c] dL g^{-1}	k_H	SEC[d] V_e	$\bar{M}_w/\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[f]
II-1-1	94.9	1.0_8	138.0	1.3_0	1.10_3	0.30	0.36_9	0.44	42.8	1.45	1.45
II-1-2	59.0	1.2_5	84.8	1.6_2	0.77_5	0.30	0.29_2	0.54	44.5	1.44	1.42
II-2	37.4	1.8_5	53.0	1.5_9	0.54_6	0.32	0.23_0	0.53	46.4	1.42	1.41
I-1	26.8	2.1_5	40.0	1.7_0	0.43_8	0.39	0.20_0	0.66	47.0	1.49	1.43
II-3	22.0	2.1_2	28.3	2.0_9	0.35_2	0.39	0.17_3	0.70	48.3	1.29	1.25
I-2	18.3	2.2_4	26.4	1.8_3	0.33_9	0.37	0.16_7	0.71	48.5	1.44	1.36
I-3	11.8	2.4_7	16.9	2.2_9	0.24_4	0.35	0.13_3	0.78	50.0	1.43	1.37
II-4	11.0	2.5_5	14.5	2.2_9	0.22_0	0.41	0.12_5	0.83	50.9	1.32	1.25
I-4	7.4_9	2.8_4	10.0	2.3_5	0.17_0	0.32	0.10_4	0.87	52.0	1.34	1.34
I-5			8.1_6	3.3_8	0.14_7	0.39	0.09_2	0.90	52.8		1.31

[a] $A_2 = 2.1_8 \times 10^{-2} \bar{M}_n^{-0.38}$. [b] $A_2 = 3.4_5 \times 10^{-2} \bar{M}_w^{-0.23}$. [c] Θ conditions; ethyl acetate, 27 °C. [d] $\log \bar{M}_w = 11.42 - 0.1234 V_e$; $\log([\eta]\bar{M}_w) = 15.14 - 0.2111 V_e$; V_e denotes peak position. [e] Absolute molecular weight measurements. [f] SEC.

Table V
Molecular Characteristics of Poly(stearyl methacrylate) (PSMA)

sample	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$,[a] mol cm^3 g^{-2}	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$,[b] mol cm^3 g^{-2}	$[\eta]_{30°C}{}^{THF}$, dL g^{-1}	k_H	$[\eta]$,[c] dL g^{-1}	k_H	SEC[d] V_e	$\bar{M}_w/\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[f]
II-1	68.4	1.6_7	93.4	1.4_9	0.94_1	0.37	0.35_7	0.56	42.7	1.38	1.38
II-2	40.2	1.7_7	51.3	2.2_6	0.66_5	0.40	0.27_5	0.63	44.2	1.28	1.27
I-1	28.3	2.21	37.9	2.6_7	0.52_6	0.36	0.21_3	0.74	45.5	1.34	1.34
I-2	18.7	2.1_7	28.9	2.9_3	0.37_7	0.46			46.7	1.54	1.31
II-4	19.0	2.4_5	21.1	2.8_0	0.33_8	0.39	0.17_6	0.67	47.5	1.11	1.23
I-3	13.4	2.8_0	16.3	3.2_0	0.26_7	0.49	0.14_6	0.72	48.4	1.22	1.24
II-5	10.5	2.7_4	13.5	3.7_9	0.23_3	0.45			48.6	1.29	1.25
I-4	7.7_3	3.1_9	9.1_8	3.8_8	0.18_5	0.51	0.11_2	0.84	50.5	1.19	1.22
II-6	5.0_6	3.2_9	6.8_5	5.6_4	0.14_9	0.46			52.2	1.35	1.30
I-5	3.3_8	4.2_3	4.4_4	4.7_1	0.114	0.67	0.07_9	0.99	53.4	1.30	1.28
I-6			1.5_3	$11._1$	0.06_1	1.45			57.2		1.28

[a] $A_2 = 0.89 \times 10^{-2} M_n^{-0.30}$. [b] $A_2 = 0.48 \times 10^{-2} M_w^{-0.41}$. [c] Θ conditions; *n*-propyl acetate, 36 °C. [d] $\log \bar{M}_w = 11.13 - 0.1214 V_e$; $\log([\eta]\bar{M}_w) = 14.48 - 0.2016 V_e$; V_e denotes peak position. [e] Absolute molecular weight measurements. [f] SEC.

Table VI
Molecular Characteristics of Poly(docosyl methacrylates) (PDCMA)

sample	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$,[a] mol cm^3 g^{-2}	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$,[b] mol cm^3 g^{-2}	$[\eta]_{30°C}{}^{THF}$, dL g^{-1}	k_H	$[\eta]$,[c] dL g^{-1}	k_H	SEC[d] V_e	$\bar{M}_w/\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[f]
II-1	96.0	1.3_6	135.0	1.4_3	0.85_6	0.44	0.47_2	0.47	42.4	1.41	1.33
II-2	83.0	1.4_6	114.0	1.6_0	0.77_0	0.39	0.43_6	0.42	43.1	1.37	1.28
II-3	57.7	1.6_8	70.8	1.7_7	0.57_3	0.37	0.33_5	0.37	44.8	1.23	1.24
III-1	40.6	1.9_4	53.1	1.9_5	0.46_8	0.37	0.28_7	0.34	46.1	1.31	1.28
II-4	33.6	1.9_7	45.8	1.9_8	0.41_7	0.48	0.27_0	0.40	46.8	1.36	1.27
III-2	21.7	2.2_9	31.5	1.9_4	0.34_7	0.41	0.21_4	0.53	47.6	1.45	1.28
II-5	19.1	2.4_5	26.0	2.2_7	0.28_9	0.48	0.19_7	0.41	49.1	1.36	1.33
III-3	16.1	2.5_9	22.8	2.3_8	0.27_2	0.42	0.18_3	0.39	49.4	1.42	1.31
III-4	11.1	3.6_0	14.7	2.7_9	0.20_3	0.46	0.14_5	0.38	50.9	1.32	1.25
III-5	7.1_0	4.0_4	10.3[f]		0.16_0	0.51	0.12_3	0.40	52.3		1.25
III-6	3.9_2	6.7_3	5.6_8[f]		0.11_8	0.62			54.6		1.35

[a] $A_2 = 3.0_0 \times 10^{-2} \bar{M}_n^{-0.39}$. [b] $A_2 = 6.3_4 \times 10^{-2} M_w^{-0.27}$. [c] Near Θ conditions; amyl acetate, 31 °C. [d] $\log \bar{M}_w = 10.86 - 0.1116 V_e$; $\log([\eta]\bar{M}_w) = 13.98 - 0.1867 V_e$; V_e denotes peak position. [e] Absolute molecular weight measurements. [f] SEC.

The intrinsic viscosity $[\eta]$ and weight-average molecular weight data (Tables III–VI) yield the usual Mark–Houwink–Sakurada (MHS) relationships under both ideal and nonideal conditions, the parameters of which are presented in Table VII. The exponent values of 0.50 found for PDMA, PTDMA, and PSMA fortify the light scattering Θ-temperature measurements. The evaluation of the Θ temperature for PDCMA was not accomplished as a result of sample precipitation in amyl acetate prior to reaching the zero value for the second virial coefficient. As a consequence the unperturbed chain posture was determined at 31 °C—a temperature at which light scattering and intrinsic viscosity results demonstrated the lack of chain aggregation over the evaluated concentration range. The MHS exponent of 0.53 shows that the intrinsic viscosity measurements were done at a temperature that can be classified as near-Θ. The K_Θ parameter was then evaluated by utilizing the extrapolation procedure developed by Burchard[20] and Stockmayer and Fixman[21].

The preexponential terms (the K_Θ values of Table VII) of the MHS relationships are used to determine the unperturbed dimensions $\langle r^2 \rangle_0$ according to Flory's equation

$$K_\Theta = \Phi[\langle r^2 \rangle_0 / M]^{3/2} \qquad (1)$$

where Φ, the Flory constant, has been found experimentally[32-38] to have the value of 2.5 (±0.1) × 10^{21}. Prior, though, to the determination of the $[\langle r^2 \rangle_0/M]^{3/2}$ ratio, the experimental value of K_Θ should be altered by a factor designed to correct for polydispersity. The presence of polydisperse molecular weight distributions, as shown by size exclusion chromatography measurements, coupled with the measured molecular weight distributions dictated the value of 1.03 for the correction factor. Although small, this correction factor was applied to the experimental values of K_Θ.

Table VII
Mark–Houwink–Sakurada Relationships for Poly(*n*-alkyl methacrylates)

sample	THF, 30 °C		Θ conditions		Θ solvent	Θ temp, °C
	$K \times 10^5$	α	$K_\Theta \times 10^4$	α		
PDMA	4.56	0.73	3.47	0.50	ethyl acetate	11
PTDMA	4.74	0.71	3.22	0.50	ethyl acetate	27
PSMA	8.95	0.67	3.71	0.50	*n*-propyl acetate	36
PDCMA	1.05	0.64	3.66	0.53[a]	amyl acetate	31[a]

[a] Slightly above the Θ temperature; see text.

The characteristic ratio, C_∞, as defined by Flory[2] relates the unperturbed root-mean-square end-to-end distance to chain length—the latter being expressed in terms of the number of chain bonds, n, and the square of the average bond length, l^2. This dimensionless ratio serves as a measure of the unperturbed posture of a polymer chain and is given as follows:

$$C_\infty = \langle r^2 \rangle_0 / n l^2 \qquad (2)$$

The C_∞ values for the poly(*n*-alkyl methacrylates) examined in this work are given in Table VIII along with values available from a previous compilation.[39] The results in Table VIII show that an increase in length of the *n*-alkyl side group leads to a concomitant enhancement in C_∞ for *n*-alkyl methacrylate polymers of essentially identical tacticity. Clearly, the increase in C_∞ is a reflection of the influence exerted by the *n*-alkyl unit on the conformational characteristics of the chain in question.

As Flory and co-workers[40,41] have pointed out the $\bar{g}$ conformations are virtually absent from disubstituted vinyl

Table VIII
Characteristic Ratios of Poly(*n*-alkyl methacrylates)

sample[a]	$K_\theta \times 10^4$,[b] (g mol wt)$^{-1/2}$	C_∞	ref
PMMA		5.7–8.1	39
PEMA		7.6–8.0	39
PBMA		7.9–8.5	39
PHMA		10.1–10.5	39
POMA		9.6–10.4	39
PDMA	3.57	13.0	this work
PDDMA		12.9–13.4	39
PTDMA	3.32	14.7	this work
PSMA	3.82	20.4	this work
PDCMA	3.79[c]	23.6	this work

[a] The polymers not previously identified are as follows: PMMA, poly(methyl methacrylate; PEMA, poly(ethyl methacrylate); PBMA, poly(*n*-butyl methacrylate); PHMA, poly(*n*-hexyl methacrylate); POMA, poly(*n*-octyl methacrylate); PDDMA, poly(dodecyl methacrylate). [b] Corrected for polydispersity. [c] Obtained via the Burchard–Stockmayer–Fixman extrapolation procedure.[20,21]

chains such as poly(methyl methacrylate). This is a consequence of the planar nature of the ester group which leads to steric overlaps involving either of the oxygen atoms. This steric interference is independent of the rotational states of the neighboring bonds in the chain. Thus the energetically accessible conformers are limited to the t and g forms, i.e., tt, tg, gt, and gg, for the poly(methyl methacrylate) chain.

The introduction of long-chain *n*-alkyl groups also introduces an additional complicating factor regarding the chain posture of poly(*n*-alkyl methacrylate) chains. This involves the spatial configurations of the side chain itself. For example, the characteristic ratio of an *n*-alkyl chain approximately doubles[42] in going from C_{10} to C_{22}. This change in side-chain configuration would be expected to increase the number of repulsions between nonbonded atoms. The influence of these changes in side-group configuration on first-order, second-order, and higher order interactions in a disubstituted chain such as in the poly(*n*-alkyl methacrylates) is a topic that has not yet been addressed by the application of the RIS approach.

Our results can be interpreted that increasing the length of the *n*-alkyl group leads to a decrease in the population of the gauche conformers and a concurrent increase in the trans forms. In a qualitative sense, the onset of more pronounced higher order interactions would be anticipated to lead to an increase in the population of the trans conformers. As has been pointed out[40] higher order interactions are not averted for these disubstituted chains, as they are for monosubstituted vinyl chains, by an increase in interactions of the second order.

A potential additional contributing factor to the alteration of poly(*n*-alkyl methacrylate) flexibility is the interaction of the longer side chains. It has been suggested[43,44] that such interactions could lead to orientationally ordered structures. Thus, interactions between lateral chains could, at least in part, cause the observed increase in C_∞ as a function of side-chain length. In this case the application of the RIS method would not consist exclusively of calculating energy maps for the main-chain bonds. Obviously, though, detailed insight into the spatial characteristics of these poly(*n*-alkyl methacrylates) must await the application of RIS calculations.

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Registry No. PDMA (homopolymer), 29320-53-4; PTDMA (homopolymer), 41630-11-9; PSMA (homopolymer), 25639-21-8; PDCMA (homopolymer), 27252-90-0.

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