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Synthesis and chain flexibility of poly(cyclohexylethyl methacrylate)

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Summary

The synthesis and characterization of fractions of poly(cyclohexylethyl methacrylate) (PCHEM) are reported. A combination of low-angle laser light scattering and intrinsic viscosity experiments was employed to estimate the characteristic ratio (C_∞) of this polymer. The value of 10.7 obtained for PCHEM is similar to the value of 11.3 found previously for poly(phenylethyl methacrylate) but is smaller than values measured for poly(cyclohexyl methacrylate) and poly(cyclohexylmethyl methacrylate) (C_∞ = 11.6 and 11.9, respectively).

Introduction

In recent work, we investigated the influence of alkylene spacers on the conformational properties of polymethacrylates having both aryl (1) and cycloalkyl (2) substitutents. Among other observations, it was found that incorporation of a single methylene spacer into poly(alicycylmethyl methacrylates) was sufficient to cause the chain flexibility of these materials to become indistinguishable from that observed for poly(n-alkyl methacrylates) having the same number of carbons (2, 3). This was interpreted as the effect of increased ease of rotation about main chain bonds as the bulky cycloalkyl groups (which lead to diminished flexibility when bonded directly to the ester group) are moved further away from the backbone. For a series of poly(aryl methacrylates) (phenyl, benzyl, phenylethyl, and phenylbutyl derivatives), it was found that chain flexibility increased very substantially on incorporating a single methylene spacer (e.g. phenyl versus benzyl) and then gradually decreased as longer alkyl spacers were incorporated (1, 3). As with the cycloalkyl materials, the initial increase in flexibility was attributed to the influence of moving the rigid and bulky phenyl substituent away from the backbone. Upon increasing the length of the spacer (ethyl and *n*-butyl spacers), a gradual decrease in flexibility is then observed due to the overall increasing size of the substituents (1).

In this paper, we report the synthesis, fractionation, and characterization of poly(cyclohexylethyl methacrylate) (PCHEM). The chain stiffness of this polymer is evaluated through a combination of light scattering and intrinsic viscosity measurements.

Experimental

2-Cyclohexylethanol (Aldrich) was reacted with methacrylic acid in refluxing toluene using p-toluene sulfonic acid as catalyst and methylene blue as inhibitor. The progress of the esterification was monitored, based on evolution of water, using a calibrated Dean-

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Stark trap. The monomer was purified by vacuum distillation, and the structure was confirmed by ^{1}H-NMR and GC-MS.

Three free radical polymerizations of the monomer were conducted under vacuum (10^{-6} mm Hg) in sealed glass vessels using 10% (w/w) solutions of the monomer in benzene. Azobisisobutyronitrile (recrystallized from methanol) was used as initiator at levels of about 0.015, 0.10, and 0.47% (based on monomer weight). The polymerizations were run for about 2 - 4 days in a constant temperature (50°C) bath. This resulted in monomer conversions of around 50%. Polymers were isolated by precipitation into methanol, followed by vacuum drying.

Each whole polymer was separated into 4 - 6 fractions using classical solvent/nonsolvent fractionation procedures (2) with toluene as solvent and methanol as nonsolvent. Size exclusion chromatography (SEC) experiments were performed in tetrahydrofuran (THF) at 30°C using two Waters linear ultrastyragel columns. A calibration based upon >12 commercial polystyrene standards was used to evaluate the polydispersities (M_w/M_n and M_z/M_w;, ratio of, respectively, weight-to-number and z-to-weight average molecular weights) of the fractions and to obtain approximate information about their molecular weights. Based upon approximate molecular weights, polydispersity, and sample quantity, eight fractions were chosen for subsequent dilute solution characterization.

Since higher alcohols were previously found to be theta solvents for chemically similar polymethacrylates (2, 3), the series of 1-butanol to 1-heptanol was investigated in this work. Cloud point determinations on a 0.1% (wt./wt.) solution in 1-pentanol of a PCHEM fraction having molecular weight around 10^6 gave a cloud point of 20°C, suggesting that this solvent is a theta solvent slightly above room temperature. The specific refractive index increment, dn/dc, was measured in this solvent (>99.5% pure by GC) at 30°C and 633 nm as 0.099 mL g^{-1}, using an Otsuka double beam differential refractometer. Low-angle laser light scattering (LALLS) experiments were conducted using a Chromatix KMX-6 photometer at 24.5°C. The data were fit to plots of $KC/\Delta R_\theta$ versus C, where K is the "optical constant", C is polymer concentration, and ΔR_θ is the excess Raleigh ratio determined at an angle of about 6°. M_W (absolute weight-average molecular weight) and A_2 (second virial coefficient) were derived from, respectively, the intercept and slope. A_2 values near zero confirmed 24.5°C as a theta or near-theta condition for PCHEM in 1-pentanol.

Intrinsic viscosity $[\eta]$ measurements were carried out in THF at 30°C and in 1-pentanol at 24.5°C using Ubbelohde dilution viscometers having negligible kinetic energy corrections. $[\eta]$ values were derived from linear plots of η_{sp}/C versus C (η_{sp} = specific viscosity) at four polymer concentrations chosen to give η_{sp} values between about 0.1 and 0.4. Huggins coefficients, k_H, were derived from the slopes of these plots (k_H = slope/$[\eta]^2$).

Results and Discussion

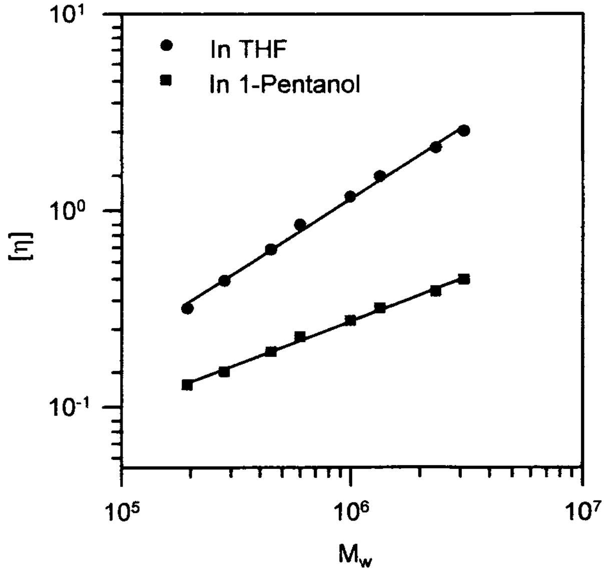
Molecular characteristics of the PCHEM fractions are summarized in Table 1. The fractions cover a broad range of molecular weights and exhibit quite narrow and symmetrical molecular weight distributions, with average M_w/M_n values of around 1.3, and average M_z/M_w values of about 1.2. THF is a thermodynamically good solvent based on the large $[\eta]$ values measured. Although not shown in Table 1, k_H values in this solvent were all about ⅓, as expected for linear flexible chains in thermodynamically good solvents (4). The [η] values obtained by the use of the theta solvent are smaller than those values in THF, but the k_H values are much larger, in accord with theory (5) and experiments on related polymers (1, 2, 6, 7).

Table 1: Molecular Characteristics of PCHEM Fractions

$M_w \times 10^{-5(a)}$	$M_w/M_n^{(b)}$	$M_z/M_w^{(b)}$	[η], dL $g^{-1(c)}$	[η], dL $g^{-1(d)}$	$k_H^{(d)}$
1.93	1.23	1.19	0.319	0.130	1.09
2.79	1.29	1.16	0.441	0.152	1.07
4.45	1.29	1.29	0.635	0.192	1.00
5.96	1.25	1.20	0.846	0.229	1.03
9.89	1.21	1.14	1.17	0.277	0.93
13.3	1.15	1.16	1.48	0.321	1.05
23.5	1.36	1.32	2.08	0.390	0.90
31.0	1.39	1.27	2.52	0.448	0.89

a) LALLS
b) SEC
c) THF, 30°C
d) 1-Pentanol, 24.5°C

Figure 1: Mark-Houwink-Sakurada Plot for Poly(cyclohexylethyl methacrylate)



The M_w and [η] data of Table 1 are plotted in Figure 1 and lead to the following Mark-Houwink-Sakurada equations:

$$[\eta] = 4.22 \times 10^{-5}\, M_w^{0.74} \text{ (THF, 30 °C)} \tag{1}$$

$$[\eta] = 5.9 \times 10^{-4}\, M_w^{0.45} \text{ (1-pentanol, 24.5 °C)} \tag{2}$$

The exponent of 0.45 in the case of 1-pentanol indicates that the intrinsic viscosity experiments were carried out slightly below the theta temperature. Therefore, unperturbed dimensions were estimated (Figure 2) by treating both the THF and 1-pentanol data using the Burchard-Stockmayer-Fixman method (8, 9). Figure 2 gives the intercept, K_θ, as $= 3.12 \times 10^{-4}$ dL g^{-1}. To correct for the slight effect of polydispersity, this K_θ value is multiplied by 1.03 (10) resulting in $K_\theta = 3.21 \times 10^{-4}$ dLg^{-1}. Flory's characteristic ratio, C_∞, may be computed using the equations (11):

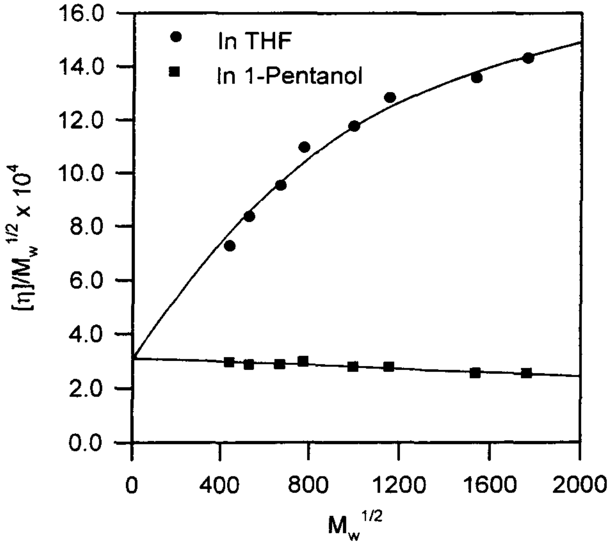
$$K_\theta = \Phi_0 \left(\langle r^2\rangle_0 / M_w\right)^{3/2} \tag{3}$$

and

$$C_\infty = \lim_{n\to\infty}\left(\langle r^2\rangle_0 \big/ nl^2\right) \tag{4}$$

where Φ_0 is the Flory hydrodynamic parameter (taken as 2.5×10^{21} mol^{-1}), $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance, and n is the number of main chain bonds of length l.

Figure 2: Burchard-Stockmayer-Fixman Plot for PCHEM



The C_∞ value of 10.7 for PCHEM derived from these data may be compared with results for related polymers. For poly(phenylethyl methacrylate), a structurally very similar material, C_∞ = 11.3 has been reported (1). These values may be considered to be nearly the same within experimental error (±5%). On the other hand, the C_∞ value of PCHEM reported herein is slightly smaller than the values of 11.6 and 11.9, respectively, reported previously for poly(cyclohexyl methacrylate) (3) and poly(cyclohexylmethyl methacrylate) (2). The smaller C_∞ value for PCHEM appears to reflect greater chain flexibility brought about by diminished steric hindrance to rotation of backbone bonds upon moving the bulky cyclohexyl substituent further away from the backbone. A reliable value of C_∞ for poly(n-octyl methacrylate) is apparently not available for comparison, but based on interpolation of data for other poly(n-alkyl methacrylates) nearly identical C_∞ values are expected for this polymer and PCHEM. This observation supports the earlier conclusion (2) that a single methylene spacer between the alicyclic substituent and the ester linkage is enough to reduce C_∞ values of methacrylates having pendant cycloalkyl substituents to the range expected for n-alkyl derivatives, minimizing the effect of the ring. Of course, the fact that the size of the ring is smaller than that of the *n*-alkyl chain having the same number of carbons, may also play a role (3).

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References

1. Chen Y-J, Mays J W, Hadjichristidis N (1994) J Polym Sci, Polym Phys Ed, 32: 715
2. Pateropoulou D, Siakali-Kioulafa E, Hadjichristidis N, Nan S, Mays J W (1994) Macromol Chem Phys, 195:173
3. Xu Z, Hadjichristidis N, Fetters L J, Mays J W (1995) Adv Polym Sci, 120:1
4. Muthukumar M, Freed K F (1977) Macromolecules, 10:899
5. Bohdanecky M, Kovar J (1982) Viscosity of Polymer Solutions, Elsevier, Amsterdam
6. Mays J W, Nan S, Wan Y, Li J, Hadjichristidis N (1991) Macromolecules 24:4469
7. Siakali-Kioulafa E, Hadjichristidis N, Mays J W (1989) Macromolecules 22:2059
8. Burchard W (1961) Makromol Chem 50:20
9. Stockmayer W H, Fixman M (1963) J Polym Sci, Part C, 1:137
10. Bareiss R E (1975) In: Brandrup T, Immergut E H (eds) Polymer Handbook, 2nd edn, Wiley-Interscience, New York, section IV
11. Flory P J (1969) Statistical Mechanics of Chain Molecules, Interscience, New York