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Solution Properties and Chain Flexibility of Poly(thiolmethacrylates). 2. Poly(cyclohexyl thiolmethacrylate)

Nikos Hadjichristidis,[1a] Costas Touloupis,[1a] and L. J. Fetters*[1b]

Department of Industrial Chemistry, The University of Athens, Athens 144, Greece, and Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

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ABSTRACT: The dilute-solution properties of eight poly(cyclohexyl thiolmethacrylate) (PTCy) fractions covering the molecular weight ($\bar{M}_w$) range 4.8×10^5 to 5.9×10^5 ($\bar{M}_w/\bar{M}_n \simeq 1.4$) were studied in tetrahydrofuran, toluene, and cyclohexane. The unperturbed dimensions were calculated by using light scattering and intrinsic viscosity data. The results indicate that PTCy is a less extended chain than poly(cyclohexyl methacrylate).

The importance of the influence of the side groups on dilute-solution polymer behavior is well documented. In the case of polymethacrylates interest has centered on the changes induced by altering the identity of the side-group substituents.[2-5] The corresponding poly(thiolmethacrylates) have received no attention except[6,7] for poly(phenyl thiolmethacrylate) (PTPh) and poly(o-methylphenyl thiomethacrylate). The dilute-solution properties of these poly(thiolmethacrylates) indicated that their chains are more flexible than poly(phenyl methacrylate).

In this paper, solution properties of poly(cyclohexyl thiolmethacrylate) (PTCy), $-CH_2C(CH_3)(COSC_6H_{11})-$, in tetrahydrofuran (THF), toluene, and cyclohexane are presented, and the results obtained are compared with those[2] for poly(cyclohexyl methacrylate) (PCy).

Experimental Section

Cyclohexyl thiolmethacrylate was prepared by reaction of methacryloyl chloride with cyclohexyl mercaptan in aqueous sodium hydroxide solution. Purification of this monomer was achieved by repeated distillation under reduced pressure [102–103 °C (5 mmHg)] in the presence of iodine as an inhibitor. The monomer yield was ca. 50%. Composition analysis yielded the following. Calcd for $C_{10}H_{16}OS$ (184.3): C, 65.17; H, 8.75; O, 8.68. Found: C, 64.9; H, 8.7; O, 8.7. The purity of the monomer, by gas chromatography, was found to be virtually 100%. Two polymerizations of cyclohexyl thiolmethacrylate were carried out at 50 °C in benzene solution (10% w/w) under vacuum ($\sim 10^{-6}$ mmHg) in the presence, respectively, of 0.01 and 0.05% (w/w) of 2,2′-azobis(isobutyronitrile).

The polymer microtacticity was determined from the ^{1}H NMR spectrum of PTCy in o-dichlorobenzene (20% w/w) at 120 °C with a Varian 300-MHz spectrometer. The percentage of isotactic (mm), atactic (mr), and syndiotactic (rr) triads was, respectively, 14, 38, and 48%. These values are virtually the same as those found[2] for PCy; thus the replacement of oxygen by sulfur does not alter the microtacticity of polymethacrylates obtained by radical polymerizations.

The fractionation was carried out in toluene/methanol in the way previously described.[5] The polydispersity of the fractions was estimated by gel permeation chromatography with THF as the solvent at 35 °C. A Waters Ana-Prep instrument was used with a differential refractive index detector. A seven-column Styragel set (total length of 28 ft) with a continuous porosity range of 2×10^3 to 5×10^6 Å was used for this analysis. The characteristics of this column arrangement are presented elsewhere.[8,9] The polydispersity indices were determined by the method of Benoit et al.[10] with the following Mark–Houwink relations ([η] in dL g^{-1}): $[\eta] = 1.02 \times 10^{-4}\bar{M}_w^{0.73}$ (polystyrene)[11] and $[\eta] = 4.07 \times 10^{-5}\bar{M}_w^{0.74}$ (PTCy) (this work). The calculations were done with an IBM 370/158 computer. The polydispersity values $(\bar{M}_w/\bar{M}_n)_{GPC}$, corrected for diffusion spreading,[12] are given in Table I and agree well with those determined by light scattering and osmometry.

The solvents used for dilute-solution measurements were reagent grade materials. Toluene and cyclohexane were fractionally distilled over calcium hydride, while THF was dried over calcium hydride and then fractionally distilled over sodium.

Light scattering measurements were carried out in a Sofica PGD instrument at 25 °C in cyclohexane with unpolarized light at 436 nm [$R_{C_6H_6}{}^{90°} = 48.4 \times 10^{-6}$ cm^{-1}].[13] The refractive index increment, dn/dc, measured under the same conditions was $(140 \pm 2) \times 10^{-3}$ cm^3 g^{-1}. A Hewlett-Packard 503 osmometer (S and S-08 membranes) was used for osmotic pressure measurements in toluene at 37 °C. Intrinsic viscosities, in THF at 35 °C and cyclohexane at 25 °C, were determined with Cannon-Ubbelohde viscometers having negligible kinetic energy corrections.

The values for the weight- and number-average molecular weights, second virial coefficients, z-average root-mean-square end-to-end distance $\langle r_z^2\rangle^{1/2}$, and intrinsic viscosities are given in Table I.

Results and Discussion

Figure 1 shows conventional log–log plots of [η] against $\bar{M}_w$ for PTCy in THF and cyclohexane. The following relationships were obtained by least-squares analyis for the two solvents used ([η] in dL g^{-1}):

$$[\eta]_{THF}{}^{35°C} = 4.07 \times 10^{-5}\bar{M}_w^{0.74}$$

$$[\eta]_{C_6H_{12}}{}^{25°C} = 8.65 \times 10^{-5}\bar{M}_w^{0.63}$$

It should be noted that if the Mark–Houwink exponent is greater than ca. 0.8, the relationship between intrinsic viscosity and molecular weight will yield[14-16] incorrect values of K_Θ and, in turn, of the unperturbed dimensions. The foregoing intrinsic viscosity–molecular weight relations show that the Mark–Houwink exponents fall within the acceptable range.

The relation between chain dimensions, in terms of the root-mean-square end-to-end distance and molecular weight for PTCy in cyclohexane at 25 °C, is shown in Figure 2. The best-fit line is given as

$$(\langle r_z^2\rangle)^{1/2} = 0.395\bar{M}_w^{0.55}$$

The value of the exponent, 0.55, agrees well with the calculated value of 0.54. The latter value results from the use of the Mark–Houwink exponent α in the relation[17] $(\alpha + 1)/3$.

The dependence of the osmometric and light scattering second virial coefficients is shown in Figure 3. The relations found are as follows:

$$A_2 = 7.3 \times 10^{-3}\bar{M}_n^{-0.27} \text{ (osmometry, toluene, 37 °C)}$$

$$A_2 = 3.2 \times 10^{-3}\bar{M}_w^{-0.26}$$
(light scattering, cyclohexane, 25 °C)

The foregoing exponents are comparable to values reported[18-24] for a variety of flexible polymers in moderate to good solvents and are consistent with theory,[25] which predicts a limiting value of −0.2 for very large molecular weights in very good solvents.

The application[26] of the Burchard–Stockmayer–Fixman plot,[27,28] Figure 4, for the [η]–$\bar{M}_w$ data in cyclohexane and THF yields the parameter K_Θ, which in this case is equal

Table I
Characterization Data for Poly(cyclohexyl thiolmethacrylate)[a]

	solvent	temp, °C	F1	F2	F3	F4	F5	F6	F7	F8
$[\eta]$, dL g^{-1}	THF	35	0.737	0.565	0.342	0.314	0.294	0.239	0.185	0.115
	cyclohexane	25	0.370	0.294	0.189	0.178	0.158	0.146	0.110	0.077
$\bar{M}_w \times 10^{-6}$			0.593	0.410	0.208	0.193	0.160	0.134	0.089	0.048
$(\langle r_z^2\rangle)^{1/2}$, A	cyclohexane	25	580	470	330	310	290	250	205	
$A_2 \times 10^4$, mL mol g^{-2}			1.1	1.0	1.2	1.4	1.5	1.4	1.6	2.0
$\bar{M}_n \times 10^{-6}$			0.450	0.293	0.150	0.142	0.122	0.095	0.069	0.035
$A_2 \times 10^4$, mL mol g^{-2}	toluene	37	1.8	2.0	2.2	2.4	2.6	2.6	3.1	3.7
$(\bar{M}_w/\bar{M}_n)_{GPC}$	THF	35	1.4	1.4	1.4	1.5	1.4	1.4	1.3	1.3
$\bar{M}_w/\bar{M}_n$			1.3	1.4	1.4	1.4	1.3	1.4	1.3	1.4

[a] F1-F8 are the various PTCy fractions, $[\eta]$ is the intrinsic viscosity, $(\langle r_z^2\rangle)^{1/2}$ is the end-to-end distance, $(\bar{M}_w/\bar{M}_n)_{GPC}$ is the polydispersity from GPC, and $\bar{M}_w/\bar{M}_n$ is the polydispersity from light scattering and osmotic pressure.

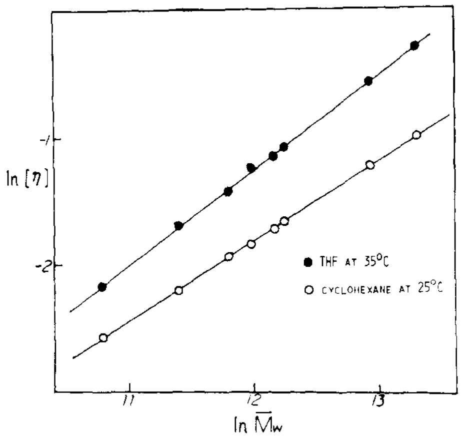

Figure 1. Intrinsic viscosity-weight-average molecular weight plots for poly(cyclohexyl thiolmethacrylate).

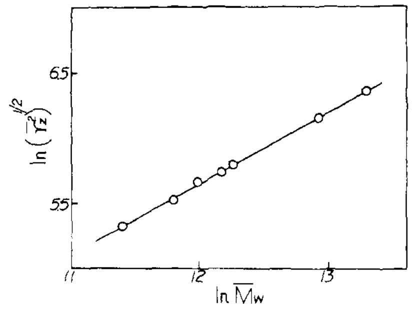

Figure 2. End-to-end distance-weight-average molecular weight plot for poly(cyclohexyl thiolmethacrylate) in cyclohexane.

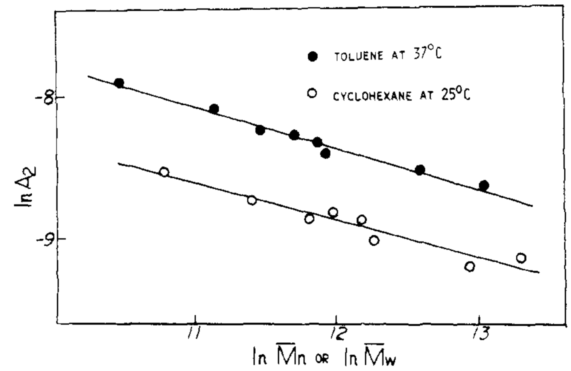

Figure 3. Second virial coefficient-molecular weight plots for poly(cyclohexyl thiolmethacrylate).

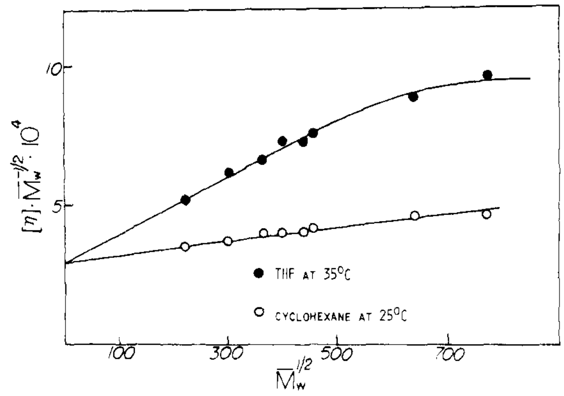

Figure 4. Burchard-Stockmayer-Fixman plots for poly(cyclohexyl thiolmethacrylate in tetrahydofuran and cyclohexane.

to 2.90 × 10^{-4} dL g^{-1}. The value of K_Θ can then be used to determine the unperturbed dimension $\langle r_0^2\rangle$, according to Flory's well-known equation

$$K_\Theta = \Phi(\langle r_0^2\rangle/M)^{3/2}$$

where Φ is the Flory constant.[29-32]

However, prior to the exploitation of the above equation, the K_Θ value must be corrected by a polydispersity factor of about 1.04, assuming a Schulz-Flory distribution.[33] Thus, the corrected value for K_Θ is 3.0 × 10^{-4} dL g^{-1}. The value for Φ is taken as 2.5 × 10^{21}. This value is the one determined from light scattering by McIntyre[34] and Berry[35] and very recently by Miyaki et al.[36] Hence, the relation between $\langle r_0^2\rangle^{1/2}$, in Å, and molecular weight is

$$\langle r_0^2\rangle^{1/2} = 0.49\bar{M}^{1/2}$$

The flexibility factor, σ, is defined as

$$\sigma = (\langle r_0^2\rangle/\langle r_{0f}^2\rangle)^{1/2}$$

where σ represents the effect of local interactions on chain flexibility and $\langle r_{0f}^2\rangle$ is the mean-square end-to-end distance, assuming completely free rotation around the carbon-carbon bonds of the polymer chain. For this case, the calculated[5] value of $\langle r_{0f}^2\rangle$ is

$$\langle r_{0f}^2\rangle^{1/2} = 0.23\bar{M}^{1/2}$$

Hence, σ for PTCy is calculated to be 2.13.

For a comparison of the average dimensions of random-coil chains, the characteristic ratio, C_∞, of Flory is used. This is defined[37] as

$$C_\infty = \lim_{n\to\infty} [\langle r_0^2\rangle/(nl^2)]$$

where n is the number of bonds in the polymer chain [$n = 2(M/m_0)$] and l is the bond length (1.55 Å). Table II summarizes the pertinent data characterizing PTCy and PCy.[2]

For purposes of comparison the K_Θ value for PCy has been corrected for polydispersity and the corresponding unperturbed dimensions have been calculated by using the

Table II
Molecular Characteristics for Poly(cyclohexyl thiolmethacrylate) and Poly(cyclohexyl methacrylate)

	PTCy	PCy[a]
microtacticity (rr in %)	48	51
$K_\Theta \times 10^4$, dL g^{-1}	3.0	4.5
$(\langle r_0^2\rangle/\overline{M})^{1/2}$ (A) (intrinsic viscosity)	0.49	0.56
$(\langle r_{0f}^2\rangle/\overline{M})_0^{1/2}$ (Å)	0.23	0.24
$(\langle r_z^2\rangle/\overline{M}_w)_0^{3/2}$ (Å^3) (light scattering)	0.26	0.35[b]
$(\langle r_0^2\rangle/\overline{M})^{1/2}$ (A) (light scattering)	0.57[c]	0.65[c]
σ (intrinsic viscosity)	2.13	2.33[d]
σ (light scattering)	2.48	3.04
C_∞ (intrinsic viscosity)	8.5	10.2
C_∞ (light scattering)	12.4	14.8

[a] Reference 2. [b] Based on fractions C_3, C_5, and C_7 of ref 2. [c] The correction for polydispersity was made according to Kurata and Stockmayer.[38] [d] The value of σ presented elsewhere was determined by using the approximate theoretical value of Φ, 2.87×10^{21}.

experimental value of Φ of 2.5×10^{21}. From Table II it is clear that the extension of PTCy is less than that of PCy. An identical trend is seen in the comparison of the intrinsic viscosity results[6,7] involving poly(phenyl thiolmethacrylate) and poly(phenyl methacrylate).

An indication of the relative amount of chain extension exhibited by PTCy and PCy can be gained from the light scattering data available here and elsewhere[2] from cyclohexane solutions. The results, obtained by Baumann's method,[39] are compiled in Table II. There it can be seen that σ and C_∞ for PTCy and PCy are larger than the corresponding values obtained from the intrinsic viscosity measurements. We have noted that the same trend is observed from the light scattering[36,40–43] and intrinsic viscosity results[36,40,41,44] for near-monodisperse polystyrenes; i.e., the Baumann plot for data obtained in good solvents yields a larger value for $\langle r_0^2\rangle/M$ than do the corresponding data obtained under Θ conditions and the intrinsic viscosity method[27,28] of Burchard, Stockmayer, and Fixman. This observation is contrary to Baumann's original assessment.[39] It is of interest to note that the value of $\langle r_0^2\rangle/M$ for polystyrene obtained from the Burchard–Stockmayer–Fixman treatment,[27,28] using results for benzene and toluene solutions, is virtually identical with that obtained from the combined series of light scattering[34,40–43] and intrinsic viscosity[36,40,41,44] measurements under Θ conditions.

Hence, the light scattering derived values for σ and C_∞ for PTCy and PCy are, we believe, overestimates.[45] However, from a relative standpoint, these values seemingly indicate that PTCy is a more flexible, i.e., less extended, chain than PCy. As a consequence, the replacement of the ester oxygen by sulfur in the side group of polymethacrylates apparently leads to an increase in the main-chain flexibility. This would appear to be due, in the main, to a change in the local intramolecular interactions and to the greater flexibility[46] of the sulfur-containing side group.

In conclusion, a comment is perhaps in order regarding comparison of poly(cyclohexyl thiolmethacrylate) and poly(phenyl thiolmethacrylate). The former is apparently a more flexible chain than the latter,[6,7] indicating that specific interactions between aromatic side groups decrease the flexibility of the main chain. This is the anticipated effect.

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