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Unperturbed Dimensions of Poly(2-chloroethyl methacrylate)

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In a study[2] of the characteristic ratios of various long side group *n*-alkyl methacrylate polymers we had occasion to prepare a series of fractionated samples of poly(2-chloroethyl methacrylate) (PCEM). The molecular weights of these samples were measured via osmometry and low-angle laser light scattering, and their dilute solution viscosities were measured under Θ conditions and in a good solvent. The Θ-solvent data allow the determination of unperturbed dimensions in an unambiguous fashion. Since this has not been previously done for poly(2-chloroethyl methacrylate), these results are the topic of this note.

Experimental Section

The monomer was obtained from Polysciences. After purification by fractional distillation under reduced pressure (measured purity >99%), the monomer was polymerized in benzene solution under vacuum-line conditions. AIBN was the initiator of choice. Polymer fractionation was accomplished by the procedures given elsewhere.[2] The PCEM tacticity was determined via ^1H and ^{13}C NMR measurements. 1,3,5-Trichlorobenzene at 105 °C was the solvent for the ^1H NMR measurements while $CDCl_3$ at 23% was used for the ^{13}C NMR analysis. These tacticity findings are given in Table I. The listed values are in essential agreement with those previously reported[4] for poly(chloromethyl methacrylate).

Polymer molecular weights and the heterogeneity indices were determined by a combination of low-angle laser light scattering (Chromatix KMX-6), membrane osmometry (Hewlett-Packard 503), and size exclusion chromatography (Waters Ana-Prep). The light scattering measurements were done in tetrahydrofuran at 30 °C while toluene at 37 °C was used for the osmometric evaluations. The relatively low A_2 values ($\leq 10^{-4}$ mL mol g^{-2}) found from the osmometry measurements indicate that toluene is a moderately poor solvent at 37 °C.

The dn/dc for PCEM in tetrahydrofuran was found to be 0.0957 (±0.001) mL g^{-1} at 633 nm (Chromatix KMX-16). The Θ solvent was *o*-dichlorobenzene at 35.7 °C. The Θ temperature was taken as that temperature at which the light scattering second virial coefficient was zero. This was determined with the Sofica PGD photometer.

The glass transition temperature for PCEM was measured for the four highest molecular weight samples with the use of Du Pont 990 instrument. The value of 67 (±2) °C is based on extrapolation to the zero heating rate. The glass transition was the only transition found over the temperature range of ~0–150 °C.

Table I
Tacticity of Poly(2-chloroethyl methacrylate)

NMR method	triads: mm	mr + rm	rr
$^1H^a$	6	37	57
$^{13}C^b$	7	37	56

[a] The triad concentrations were determined by the intensity of the methyl group protons. [b] The triad concentrations were determined by the intensity of the carbonyl carbon.

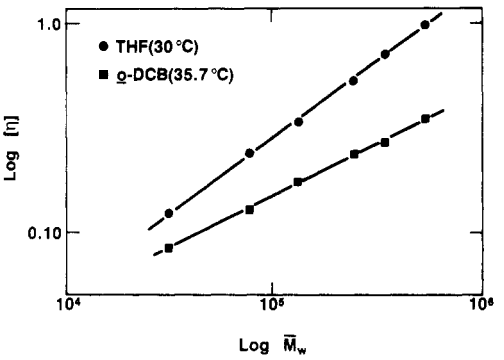

Figure 1.

Results and Discussion

Table II gives the pertinent data for the six poly(2-chloroethyl methacrylate) samples. The usual log–log plots of $[\eta]$ against $\bar{M}_w$ (Figure 1) yield the following constants for the Mark–Houwink–Sakurada (M–H–S) equations for the good solvent tetrahydrofuran (30 °C) and the Θ solvent *o*-dichlorobenzene (35.7 °C).

$$[\eta]_{THF}^{30°C} = 6.83 \times 10^{-5}\bar{M}_w^{0.72} \quad \text{(corr coef = 0.999)}$$

$$[\eta]_{o\text{-}DCB}^{35.7°C} = 4.73_8 \times 10^{-4}\bar{M}_w^{0.50} \quad \text{(corr coef = 0.999)}^5$$

The characteristic ratio[3]

$$C_\infty = \lim_{n\to\infty} [\langle r^2\rangle_0/nl^2] = \lim_{n\to\infty}\left[\frac{\langle r^2\rangle_0\bar{M}_w^{-1}}{(n'/M)l^2}\right]$$

can be obtained by the use of the familiar relation

$$K_\theta = \Phi(\langle r^2\rangle_0/\bar{M}_w)^{3/2}$$

where $\Phi = 2.5\ (\pm 0.1) \times 10^{21}$ [6-13] for intrinsic viscosities expressed in dL g^{-1}, l^2 is the mean-square average bond length, n is the number of chain bonds, n' is the number of bonds per monomer unit, and M is the monomer molecular weight.

Table II
Molecular Characteristics of Poly(2-chloroethyl methacrylate)

sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_z/\bar{M}_w$[b]	$\bar{M}_z/\bar{M}_w$[b]	$[\eta]_{THF}^{30°C}$, dL g^{-1}	k_H[c]	$[\eta]_{o\text{-}DCB}^{35.7°C}$, dL g^{-1}	k_H[c]
1	40.7	53.9	1.3_2	1.2_2	1.3_1	0.97_2	0.15	0.34_4	0.43
2	28.0	34.6	1.2_4	1.1_5	1.2_2	0.72_6	0.11	0.27_0	0.72
3	19.8	24.5	1.2_4	1.2_6	1.2_1	0.53_3	0.34	0.23_5	0.87
4	10.5	13.2	1.2_6	1.1_6	1.2_3	0.33_6	0.39	0.17_5	0.63
5	6.5_4	7.7_5	1.1_9	1.1_2	1.1_7	0.24_2	0.21	0.12_8	0.80
6	2.6_0	3.1_9	1.2_3	1.1_8	1.3_2	0.12_6	0.18	0.08_9	0.55

[a] Via absolute measurements. [b] Size exclusion chromatography; Ana-Prep. [c] Huggins coefficients.

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The Θ-condition results for PCEM yield a C_∞ value of 10.5. This value may be contrasted with those of 7.6–8.0 available[14–16] for poly(ethylmethacrylate) (PEM). Thus, the presence of the chlorine in the side chain influences the unperturbed chain dimensions of PCEM relative to PEM. A parallel effect of chlorine is seen for the case of atactic (in the Bernoullian sense) forms of poly(vinyl chloride)[17] and poly(propylene),[18] which possess characteristic ratios of 12 and 5.9, respectively, at nearly identical temperatures. Conversely, the unperturbed chain dimension behavior of poly(*p*-chlorostyrene) (C_∞ = 10.6)[19] demonstrates that the presence of chlorine exerts no influence (relative to polystyrene where C_∞ = 10.7[20,21]) when coupled with the relatively large and inflexible phenyl group.

The application of the rotational isomeric state model has shown,[22,23] the $\bar{g}$ conformations are virtually absent from poly(*n*-alkyl methacrylate) chains. The exclusion of the $\bar{g}$ conformers is the result of the planar nature of the ester group, which leads to potential steric overlaps involving one or the other oxygen atoms. This steric interference is not alleviated by an alteration of the rotational states of the neighboring bonds in the chain. Thus, *n*-alkyl methacrylate polymer chains are limited to the t and g forms as energetically accessible conformers. Our results for PCEM can be qualitatively interpreted relative to PEM, as a demonstration that the presence of the chlorine leads to an increase in the trans conformer content at the expense of the gauche conformer.

In conclusion, we wish to mention that our value of 67 (±2) °C for the glass transition is approximately 25 °C lower than the previous available value.[24] We only will note that our value for T_g is based on high molecular weight fractionated samples which did not contain residual solvent monomer or other plasticizing impurities. It is also germane to mention that poly(chloromethyl methacrylate) is reported[4] to have a T_g in the range 75–80 °C.

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Registry No. Poly(2-chloroethyl methacrylate) (homopolymer), 26937-47-3.

References and Notes

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Self-Polarizing Liquid Crystalline Films

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The theory of small-angle light scattering (SALS) from anisotropic solid materials has been described by Stein and co-workers on the basis of a model approach[1,2] as well as a statistical approach.[3,4] The former is useful for scatterers with known geometry such as spheres, disks, or rodlike structures. The latter represents a more general case without requiring any prior knowledge of the structures. SALS theory is commonly treated in various polarization configurations using a variety of combinations of a polarizer and an analyzer. These include Hv scattering (vertically polarized incident light with horizontal analyzer), Vv scattering (vertical polarizer with vertical analyzer), and Hh scattering (horizontal polarizer with horizontal analyzer).

SALS theory predicts that Hv scattering (under cross polarization) is primarily a result of orientation fluctuations while Vv scattering and Hh scattering (in parallel polarization) depend on additional contributions arising from density fluctuations as well as the polarizability of the surrounding medium. The theory has been rigorously applied to solid crystalline polymers[1–4] and recently to the superstructures forming liquid crystalline polymers.[5,6] The scattering of light from liquid crystals is found to be predominantly a consequence of orientation fluctuations. The intensity of this scattering turns out to be much greater than that arising from the density fluctuations in the nematic fluids, so much so that the latter contribution can practically be neglected. This is in accordance with the continuum theory of light scattering predicted by de Gennes.[7,8]

It is a common practice to utilize a combination of a polarizer and an analyzer in SALS experiments to specify the polarization directions of the incident electric vector and of the scattered wave. The present paper demonstrates that an anisotropic scattering pattern, characteristic of a rodlike scattering, can be obtained in a nematic liquid crystalline film without using an external polarizer or an analyzer. The material of interest is (hydroxypropyl)-

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