Effect of water and tacticity on the glass transition temperature of poly(2-hydroxyethyl methacrylate)

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Poly(2-hydroxyethyl methacrylate) (PHEMA) and related hydrogels are being studied for a variety of medical applications[1].

Several conflicting values of the glass transition temperature (T_g) of PHEMA have been reported. The range of values quoted are summarized in *Table 1*. The disagreement between the values quoted may be attributed to the large influence of sorbed moisture due to the hygroscopic nature of the materials[2]. Differences in tacticity may also be expected to affect the T_g.

In this study the T_g of PHEMA samples of different tacticities has been determined as a function of sorbed water content. The samples based on PHEMA are: (a) 58% syndiotactic, 42% heterotactic PHEMA containing 1 mol % ethylene glycol dimethacrylate (EGDMA) crosslinker and polymerized at 333K and (b) 80% isotactic, 15% heterotactic, 5% syndiotactic PHEMA polymerized at 263K without added crosslinker (preparation details are given in ref 13). The tacticities of the samples were measured by ^{13}C n.m.r. spectra[3,4,13].

The T_g data were obtained from differential scanning calorimetry (d.s.c.) thermograms using a Dupont 990 thermal analyzer and d.s.c. cell base. The instrument was calibrated with indium, tin, and triple distilled water. The T_g values measured are shown in *Figure 1*. Extrapolating linearly the portion of the graph where water content approaches zero, the T_g values are: 393 ± 2K for the 58% syndiotactic sample (a), and 311 ± 2K for the 80% isotactic sample (b).

Table 1 Reported glass transition temperatures of PHEMA

T_g(K)	Reference
308*	3
347	4
359	5, 6
363	7
366.5	8, 9
371	10
373	11,12
382†	3

* Isotactic PHEMA; † syndiotactic PHEMA

The effect of diluents (or plasticizers) on the T_g of a polymer may, for many systems, by given by[14,16]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{1}$$

where subscripts 1 and 2 refer to polymer and diluent (H_2O), respectively; W_1 and W_2 are the weight fractions of polymer and water, respectively. Equation (1) may be arranged to a more convenient form by utilizing the identity:

$$W_1 = (1 - W_2) \tag{2}$$

Thus:

$$\frac{1}{T_g} = \frac{1}{T_{g_1}} - W_2 \left(\frac{T_{g_2} - T_{g_1}}{T_{g_1} T_{g_2}} \right) \tag{3}$$

This equation states that for systems containing no water T_g is equal to T_{g_1}.

Utilizing equation (3), we can calculate the average T_g of the system PHEMA–H_2O since we know the T_g for 58% syndiotactic PHEMA (393K), for 80% isotactic PHEMA (311K) and for water (139K)[17,18]. The calculated values for PHEMA–H_2O systems are shown as the broken and full lines in *Figure 1*.

The results show that the T_g of PHEMA is markedly affected by the water content and by the stereochemistry of the polymer. This lowering of T_g is likely due to the removal of barriers to the rotational and translational motions of the PHEMA molecule chain segments due to their interactions with water molecules. The difference between the T_g of isotactic and syndiotactic PHEMA can be interpreted in terms of structure formation as follows: in the isotactic structure the steric hindrance between the bulky ester side chains can be minimized by coiling the backbone into a helical structure[3]. The syndiotactic polymer, however, may form much stiffer structures because the side chain impingement cannot be eliminated by helix formation[3]. These results correspond with the data observed for poly(methyl methacrylate) PMMA; i.e , T_g of isotactic PMMA is 316K, while that of syndiotactic PMMA is 388K[19].

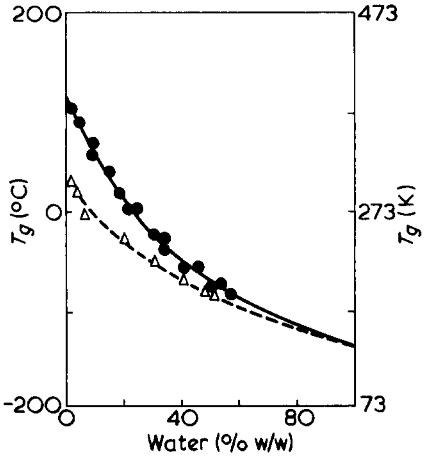

Figure 1 The glass transition temperature as a function of water content in (a) 58% Syndiotactic, 42% Heterotactic PHEMA – 1 mol % EGDMA; (b) 80% Isotactic, 15% Heterotactic, and 5% Syndiotactic PHEMA (△). The T_g of pure water is taken as 139K 139K[17,18]. The dotted and solid lines are the values calculated from equation (3)

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[η] – *M* relationship for isotactic polypropylene obtained with 'high-mileage' catalysts

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A new catalyst system, denominated 'high-mileage' (*HM*) catalyst, has been recently set up for the synthesis of isotactic polypropylene[1]. Its characteristic is that the weight ratio of polymer produced to Ti used in the catalyst system is higher by two orders of magnitude than that from traditional Ziegler–Natta catalysts (ZN).

The advantages that such new catalysts may offer in industrial practice may easily be seen, especially in view of the final polymer purification from inorganic residues.

Since the behaviour of *HM* polypropylene in some technical applications seems to differ slightly from that of the ZN polymer[2] we were led to undertake research aiming at establishing any possible structural difference by a close comparison of the two polypropylenes.

The preliminary results obtained from an investigation on dilute fraction solutions are reported in this Note.

EXPERIMENTAL

Polymer samples

Two *HM* polypropylene samples were prepared and denominated *HMa* and *HMb*. A sample, ZN 30, was chosen from polypropylene obtained in the presence of a traditional catalyst. All three samples show an intrinsic viscosity of 1.65 ± 0.01 (100 cm^3/g) in tetrahydronaphthalene at 135°C.

Fractionations

Fractionations were carried out according to the technique of the fractional solution by using a sand-packed column, which is fundamentally of the Baker–Williams type[3]. Tetrahydronaphthalene and diethyleneglycol-monoethyl ether were used as a solvent–non solvent pair. The temperature used was 145°C and atmospheric oxygen was rigorously excluded. Since the fractionation column only provided 0.05 g of the fractions, insufficient for physicochemical determinations, 6 to 8 samples from each polymer were fractionated: the fractions exhibiting quite similar [η] values were collected together to form the larger amounts necessary for measurements. These cumulative fractions were first homogenized and then subjected to a polydispersity control through gel permeation chromatography by determining the $\bar{M}_w/\bar{M}_n$ ratio.

Viscosimetry

Viscosimetric determinations were carried out by a Desreaux–Bischoff type viscosimeter, manufactured in such a way as to obtain negligible kinetic energy effects. The solvent used was tetrahydronaphthalene at 135°C.

Molecular weight determination

Measurements were carried out by a photogoniodiffusometer Sofica 50, with unpolarized light ($\lambda = 5461$ Å) using α-chloronaphthalene at 150°C as a solvent.

For calculations, use was made of $dn/dc = -0.190\ cm^3/g$ and of a Rayleigh ratio of benzene at 23°C equal to $15.8 \times 10^{-6}\ cm^{-1}$. Each fraction was measured at five different concentrations, at angles between 30° and 150°.

The linearity of the Zimm plots obtained allowed a fairly accurate molecular weight determination.

RESULTS AND DISCUSSION

The final data are reported in *Table 1*. As shown in column 3 of the Table, the fractions we used maintain a considerable polydispersity residue. This is not unexpected since our fractions actually consist of mixtures, though presumably of very similar fractions, and since only the fractionation does not generally guarantee narrow fractions, especially in the case wide-distributed raw polymers. Under such conditions, the $[\eta]-\bar{M}_w$ relationships that may be calculated for the two polymer types do not serve validly to compare the rheological and conformational behaviour of the two polypropylenes.

With regard to the fractions, by analogy with other workers[4] we think it more convenient to propose a residual molecular weight distribution of the Wesslau type[5] and then to apply the following expression:

$$\bar{M}_v = \bar{M}_w d^{-1-a/2} \tag{1}$$

Table 1 Data on *HM* and *ZN* polypropylene fractions ([η] in tetrahydronaphthalene at 135°C (100 cm^3/g); $d = \bar{M}_w/\bar{M}_n$ by gel permeation chromatography; $\bar{M}_v$ calculated from equation (1) with $a = 0.74$ and $\bar{M}_w$ by light scattering measurements)

Fractions		[η]	$d = \frac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_v \times 10^{-3}$
HMa	18	4.22	1.92	710
HMa	17	3.34	1.82	569
HMb	14	2.97	1.89	469
HMa	16	2.58	1.67	394
HMb	13	2.35	1.72	356
HMb	10	1.21	1.21	128
HMa	12	1.12	1.30	117
HMa	9	0.64	1.24	58
HMb	7	0.57	1.20	46
HMa	7	0.41	1.20	35
ZN	18	4.40	2.35	745
ZN	17	3.94	2.10	625
ZN	15	2.33	1.80	333
ZN	11	1.15	1.35	130
ZN	8	0.57	1.30	48
ZN	6	0.42	1.15	33

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