Dipole moments of isotactic and atactic poly(propylene oxide) samples

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Dipole moments of poly(propylene oxide) (PPO) samples with different tacticities were determined from dielectric constant and refractive index increment measurements, which were performed on dilute toluene and isooctane solutions. In contrast to previous reports, both refractive index increments and the dipole moment ratios showed a marked dependence on the tacticities of the samples. The dipole moment ratios of isotactic samples were greater than unity and decreased with increasing sequence concentrations of structural irregularities. The temperature coefficients in toluene were negative for both isotactic and atactic samples. No effect of excluded volume was observed.

(Keywords: poly(propylene oxide); dipole moment ratio; refractive index increment; temperature coefficient; ^{13}C nuclear magnetic resonance; tacticity; head-to-head units)

INTRODUCTION

The mean-square dipole moment of chain molecule $\langle \mu^2 \rangle$ is an important statistical average quantity that provides information regarding the spatial configuration of polymers having polar bonds. It can be determined experimentally from the dielectric constant measurements in solution or in bulk. Values of $\langle \mu^2 \rangle$ and other configuration-dependent properties may be calculated as well, using rotational isomeric state theory, from structural information and conformational energies[1].

Dipole moments of chain molecules may depend markedly on stereochemical composition. The dependence of the chain conformation and the mean-square moments of asymmetric vinyl chains on the stereochemical composition has been studied experimentally and theoretically[2–6]. The influence of the stereochemical constitution on chain statistics of some other polymers have also been reported[7–11].

Configurational characteristics of polyethers have been studied extensively[12–15]. Among them poly(propylene oxide) (PPO) has a special importance. The methyl group in the repeat unit not only gives the chain a stereochemically variable structure but it also makes the repeat unit asymmetric in the sense that the group dipole would have a component along the chain direction, which could give rise to an excluded-volume effect on the dipole moment ratio[16]. There have been only a few studies on the dipole moment of PPO[17–21], in which no significant difference was observed between the dipole moments of isotactic and atactic PPO.

However, it now appears that the terms 'tacticity' and 'stereoregularity' are unable to define the microstructural composition of PPO. For example, atactic PPO synthesized by using KOH does not contain (or scarcely contains[22]) structural irregularities (i.e. head-to-head or tail-to-tail linkages); whereas in the stereoregular PPO obtained by using Pruitt–Baggett type or organometallic catalysts, the main irregularities found in the chains are structural in type[23]. Furthermore, the so-called stereoregular PPO is a sum of polymers differing in structural regularities, which can be further split into several fractions differing in melting points, hence in the sequence concentrations of structural irregularities[24].

In this paper, we would like to report on the experimentally determined dipole moments of a series of isotactic PPO samples, which differ from each other in the sequence concentrations of structural regularities, as well as an atactic PPO synthesized by using KOH.

EXPERIMENTAL

Polymer fractions

Partially stereoregular PPO samples were synthesized by using the Pruitt–Baggett catalyst[25]. A column packed with glass beads was used to fractionate these polymers into stereoregularly uniform fractions. PPO was first crystallized on the glass beads from isooctane solution by stepwise lowering the column temperature. Each layer of PPO crystals, which were deposited in different temperature ranges, was extracted by washing the beads with isooctane. Several fractions differing in melting point (T_m) and molecular weight were obtained by progressively increasing the solvent residence time and the extraction temperature. The details of the column fractionation have been reported elsewhere[26]. In order to prevent any degradation, the PPO samples were stored in sealed ampoules under vacuum in the dark.

Atactic PPO was synthesized and isolated as described by Steiner *et al.*[27].

Polymer characterization

Melting points were measured on a hot-stage polarizing microscope. PPO solutions in benzene were put one drop at a time on a glass plate. Benzene was evaporated by blowing air. The deposited film on the glass plate was melted in an oven at about 363–373 K. The temperature of the oven was decreased gradually down to room temperature in 12–15 h. Such treated samples crystallized in the form of spherulites. On the hot stage of the

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polarizing microscope the films were heated at a rate of 0.2 K min^{-1}. The temperature at which the spherulites disappeared was noted as the bulk melting point, T_m.

Viscosity-average molecular weights (M_v) were calculated from the intrinsic viscosities measured in toluene at 298 K using the following relation[28]:

$$[\eta](\mathrm{dl\ g^{-1}}) = 1.29 \times 10^{-4} M_v^{0.75}$$

The number-average molecular weight of atactic PPO was measured cryoscopically in recrystallized benzene.

^{13}C n.m.r. spectra of the samples were recorded in C_6D_6 with proton noise decoupling using a 20.1 MHz Bruker spectrometer. Internal field frequency stabilization was provided by a lock signal from tetramethylsilane dissolved in the solvent. The peak area ratio was determined by using a Dupont 310 curve resolver.

Differential refractive index measurements

A Brice Phoenix differential refractometer was used to measure differential refractive index increments of polymer solutions at 546 nm wavelength. The optical cell was kept at constant temperature by running water from a Lauda thermostat through the jacket housing. Since the observed variations of refractive index increments with temperature (in the range of 298–313 K) remained within the experimental error limits, all the values given in *Tables 1–9* were measured at 298 K.

Dielectric constant measurements

The dielectric constant measurements were made with a capacitance bridge (General Radio Co., type 1620A) at a frequency of 10 kHz, at which the dielectric constant obtained is to a good approximation the static value. The cell used was a Balsbaugh Laboratories model 350-G three-terminal cell, which consists of two coaxial cylinders and requires about 55 cm^3 of solution. Solvent escape was prohibited and the temperature of the cell was controlled to ±0.1 K. Low-frequency dielectric increments were measured at several concentrations in the range 0.5–1.5 wt%. All the solutions were prepared by weighing both components. Measurements were carried out in toluene solutions in the range 283–333 K and in isooctane in the range 313–333 K at 5 K intervals.

RESULTS AND DISCUSSION

Sequence concentrations of structural irregularities in PPO samples

^{13}C n.m.r. spectra of the sample with the highest melting point (viz. F40, *Table 1*) consist of three absorption peaks at 17.8, 73.9 and 75.9 ppm with almost equal intensity, which were assigned to methyl, methylene and methine carbons respectively. Although methylene and methine carbon absorption peaks split into a number of peaks, as the melting points of the samples decreased, the ^{13}C n.m.r. data in this region of the field did not permit a quantitative analysis because of the mixing of the regio-regular and regio-irregular resonances[29]. The KOH polymerized atactic polymer, which does not contain (or scarcely contains) structural irregularities, like F40, gave a single absorption peak at 17.8 ppm. On the other hand, the methyl-carbon absorption peaks of lower-melting-point samples did split into two peaks. The minor peak at 18.6 ppm grew larger as the melting points of the samples decreased. Based on these observations the sequence concentrations of structurally irregular repeat units (f) were calculated[24] as the ratio of the areas of the peak at 18.6 ppm to the total area of the peaks at 17.8 and 18.6 ppm (*Table 1*).

As far as the melting point depressions of stereoregular samples are considered, the chemical identity of the irregularities are immaterial. Assuming that the irregular isomers occur randomly along the chain, their sequence concentrations (f_F) were calculated[24] from the measured melting points using Flory's formula[30]. In *Table 1*, there is a good agreement between f and f_F values. Therefore, these results confirm the previous results that the main irregularities that occur in the stereoregular PPO are of structural type[23].

Dipole moment measurements

The mean-square dipole moments per structural bond ($\langle\mu^2\rangle/x$) were calculated by using an appropriate form of Guggenheim–Smith equation[31,32]:

$$\frac{\langle\mu^2\rangle}{x} = \frac{27kTM}{4\pi\rho_1}\left(\frac{(\mathrm{d}\varepsilon/\mathrm{d}w)_0}{(\varepsilon_1+2)^2} - \frac{2n_1(\mathrm{d}n/\mathrm{d}w)_0}{(n_1^2+2)^2}\right)$$

where x is the number of skeletal bonds, M is the molecular weight per skeletal bond (that is, one-third of the monomer molecular weight), k is the Boltzmann constant, T is the absolute temperature, ρ_1 is the density of solvent, n_1 and n and ε_1 and ε are refractive indices and dielectric constants of solvent and solution respectively, w is the solute weight fraction and the subscript 0 denotes the extrapolated values at infinite dilutions. The values of n_1 and ρ_1 were taken from the literature at each temperature[33].

Table 1 Characteristics of the samples

Sample	T_m (K)	$M_v \times 10^{-3}$	f^a	$f_F{}^b$	dn/dc^c (cm^3 g^{-1})	dn/dc^d (cm^3 g^{-1})
F40	341	724	–	0.12	−0.072	0.094
F32	328	309	–	0.21	−0.062	–
F28	324	477	0.19	0.23	−0.056	–
F21	313	230	0.31	0.27	−0.035	–
F7	308	55	0.32	0.35	−0.022	–
Atactic	–	1.6^e	–	–	−0.046	0.050

[a] Sequence concentrations of structurally irregular isomers, estimated from ^{13}C n.m.r.
[b] Sequence concentrations of structurally irregular isomers, estimated from Flory's equation
[c] In toluene
[d] In isooctane at 313 K
[e] Number-average molecular weight

Results of dipole moment measurements were expressed in terms of a dimensionless dipole moment ratio[34]:

$$D_\infty = \langle\mu^2\rangle/xm^2$$

where x is the number of skeletal bonds and m^2 is the average of the squares of skeletal bond moments.The dipole moment ratio represents the factor by which the mean-square dipole moment of the actual chain departs from the freely jointed chain with the same number of bonds. The value of m^2 for PPO was calculated as follows:

$$m^2 = \tfrac{1}{3}(m^2_{\mathrm{C-C}} + m^2_{\mathrm{C-O}} + m^2_{\mathrm{O-C}})$$

in which $m_{\mathrm{C-C}}$ was taken as 0.00 D and $m_{\mathrm{C-O}} = m_{\mathrm{O-C}} =$ 1.07 D[35]. So for PPO, $m^2 = 0.76\ \mathrm{D}^2$.

The relevant experimental data and the results of dipole moment measurements in toluene in the temperature interval 283–333 K are given in *Tables 2–7*.

Table 2 Results of dipole moment measurements of sample F40 in toluene

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
283	11.71	−0.19	2.12	2.78
288	10.74	−0.19	2.00	2.62
293	10.33	−0.19	1.97	2.58
298	10.05	−0.19	1.97	2.58
303	9.77	−0.18	1.96	2.57
308	9.36	−0.18	1.92	2.52
313	9.01	−0.18	1.90	2.49
318	8.67	−0.18	1.87	2.56
323	8.44	−0.18	1.87	2.45
328	7.99	−0.18	1.82	2.38
333	7.65	−0.18	1.77	2.33

Table 3 Results of dipole moment measurements of sample F32 in toluene

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
283	11.01	−0.16	1.99	2.61
288	10.63	−0.16	1.98	2.59
293	10.17	−0.16	1.94	2.54
298	9.06	−0.16	1.77	2.31
303	7.62	−0.16	1.52	1.99
308	7.11	−0.16	1.45	1.90
313	6.43	−0.16	1.34	1.76
318	5.93	−0.16	1.26	1.66
323	5.42	−0.15	1.18	1.54
328	5.14	−0.15	1.15	1.50
333	4.68	−0.15	1.07	1.40

Table 4 Results of dipole moment measurements of sample F28 in toluene

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
283	7.64	−0.15	1.38	1.81
288	7.64	−0.15	1.41	1.86
293	7.16	−0.15	1.37	1.79
298	6.87	−0.14	1.34	1.76
303	6.55	−0.14	1.31	1.72
308	6.11	−0.14	1.25	1.64
313	5.86	−0.14	1.23	1.61
318	5.60	−0.14	1.20	1.58
323	5.16	−0.14	1.14	1.49

Table 5 Results of dipole moment measurements of sample F21 in toluene

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
283	6.64	−0.09	1.20	1.58
288	6.34	−0.09	1.19	1.56
293	6.21	−0.09	1.19	1.56
298	6.04	−0.09	1.19	1.55
303	5.81	−0.09	1.17	1.53
308	5.58	−0.09	1.15	1.51
313	5.32	−0.09	1.13	1.48
318	5.13	−0.09	1.12	1.46
323	4.90	−0.09	1.09	1.43
328	4.57	−0.09	1.04	1.36
333	4.45	−0.09	1.04	1.35

Table 6 Results of dipole moment measurements of sample F7 in toluene

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
283	5.57	−0.06	1.01	1.33
288	5.07	−0.06	0.95	1.24
293	4.93	−0.06	0.94	1.24
298	4.61	−0.06	0.90	1.18
303	4.49	−0.06	0.90	1.18
308	4.07	−0.06	0.84	1.10
313	3.94	−0.06	0.83	1.09
318	3.83	−0.06	0.83	1.09
323	3.72	−0.05	0.82	1.08
328	3.57	−0.05	0.81	1.06
333	3.34	−0.05	0.77	1.01

Table 7 Results of dipole moment measurements of atactic PPO in toluene

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
283	2.05	−0.12	0.35	0.47
288	1.98	−0.12	0.35	0.46
293	1.90	−0.12	0.35	0.46
298	1.85	−0.12	0.34	0.45
303	1.80	−0.12	0.34	0.45
308	1.68	−0.12	0.34	0.44
313	1.68	−0.11	0.34	0.44
318	1.63	−0.11	0.33	0.44
323	1.50	−0.11	0.32	0.41

The most interesting result of this study is that the D_∞ ratios for stereoregular samples are greater than unity (*Tables 2–6*). Furthermore the D_∞ ratio at a given temperature increases markedly with increasing isotacticity of the samples (i.e. decreasing f or f_{F} sequence concentrations of structural irregularities) (*Tables 2–7*).

This result clearly contradicts the preceding reports on the dipole moments of stereoregular polymers[9–11,20,21,36], where the D_∞ ratio for both tactic and atactic polymers were found to be smaller than unity.

It has been argued that, owing to the separation of substituted carbons by more than two bonds, in poly(propylene sulphide) (PPS) and PPO, the effect of stereochemical structure on statistical properties is much less pronounced in these polymers in comparison with vinyl polymers[10,11].

In spite of the earlier theoretical predictions where appreciably greater D_∞ values are expected (as large as 4–7), for tactic poly(vinyl chloride)[4], poly(*p*-chlorostyrene)[5,34] and isotactic poly(t-butyl vinyl ketone)[37], no D_∞ ratios higher than unity have been experimentally confirmed so far.

Our results are not in agreement with that of Ishikawa and Teramoto[20], who calculated the dipole moments of PPO chains with different tacticities. Considering only the steric irregularities on otherwise tactic chains, they calculated D_∞ values as 0.533, 0.616 and 0.641 for isotactic, atactic and syndiotactic chains, respectively.

On the other hand, Abe *et al.*[21] calculated the dipole moment ratios of PPO chains using the rotational isomeric states theory. Their calculations indicated an increase of D_∞ from 0.43 to 0.50 when the tacticity of PPO is changed from syndiotactic to isotactic. In this study[21], the effect of head-to-head and tail-to-tail placements (up to 10%) on the D_∞ was also examined. They calculated that the dipole moment ratio decreases with the structural irregularities but the effect was negligible up to 5%. However, their plot of D_∞ against the percentage of structural irregularities (figure 8 in ref. 21) showed a rapid decrease of D_∞ with increasing percentage of head-to-head and tail-to-tail units in the concentration range of 8–10%. The irregularities found in our samples were mainly structural isomers and their concentrations were varied between 12 and 34% (cf. *Table 1*). This might account for the decrease of D_∞ with increasing f in our samples.

However, the dipole moment ratio we found for the atactic sample ($D_\infty = 0.4$–0.5) is in good agreement with the previously reported experimental[17–19,38] and theoretical values[20,21].

This unusually high dipole moment ratio we observed for isotactic samples can be attributed to the preference of specific (presumably helical) conformation for highly isotactic PPO chains. This conformation might cause a favourable correlation between the orientation of group dipoles, resulting in a very high dipole moment for the whole chain.

For all the samples D_∞ decreases with increasing temperature in toluene in the range 283–333 K. The temperature coefficients were calculated on average to be $\mathrm{d}\ln(\langle\mu^2\rangle/x)/\mathrm{d}T = (-3.4 \pm 1.2) \times 10^{-3}\ \mathrm{K}^{-1}$ for stereoregular samples. For the atactic sample the absolute value of the temperature coefficient is smaller, viz. $\mathrm{d}\ln(\langle\mu^2\rangle/x)/\mathrm{d}T = -1.6 \times 10^{-3}\ \mathrm{K}^{-1}$, but it is still negative.

The negative temperature coefficient can be explained as follows. Increasing temperature causes disruption of low-energy rotational states, which causes helical conformations for stereoregular samples. The favourable correlation between the orientation of dipoles is lost with increasing temperature and consequently the mean-square dipole moment decreases. This also explains the relatively small temperature coefficient of the atactic sample.

It can be expected that the small dipole component of the repeat unit of PPO along the chain direction (0.18 D)[35] could give rise to an excluded-volume effect for the high-molecular-weight samples[16]. In order to see the effect of excluded volume, dipole moment measurements were also carried out in isooctane, which is a poor solvent for PPO. One highly isotactic (sample F40) and an atactic sample were studied in isooctane in the temperature range 313–333 K. The results are given in *Tables 8* and *9* respectively. Comparing the results in toluene and in isooctane, it can be seen that for the same sample at a given temperature the value of D_∞ is essentially the same in poor solvent and in good solvent. The excluded-volume effect must result in a higher D_∞ ratio in good solvent than in poor solvent. However, we did not detect such an excluded-volume effect (cf. *Tables 2*, *8* and *9*).

Table 8 Results of dipole moment measurements of sample F40 in isooctane

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
313	6.12	0.18	1.99	2.61
318	6.13	0.17	2.04	2.67
323	6.13	0.17	2.09	2.73
328	6.13	0.17	2.12	2.78
333	6.13	0.17	2.21	2.89

Table 9 Results of dipole moment measurements of atactic PPO in isooctane

Temp. (K)	$(\mathrm{d}\varepsilon/\mathrm{d}w)_0$	$2n_1(\mathrm{d}n/\mathrm{d}w)_0$	$\langle\mu^2\rangle/x$ (D^2)	D_∞
313	1.53	0.14	0.46	0.60
318	1.53	0.14	0.47	0.61
323	1.54	0.14	0.47	0.62
328	1.54	0.14	0.48	0.63
333	1.58	0.14	0.48	0.63

The small difference between the dipole moment ratios in toluene and in isooctane might be due to the fact that the correlation between the orientation of the dipoles can be more pronounced in poor solvent.The temperature coefficient for the dipole moment ratio appeared to be positive in isooctane for both isotactic and atactic samples. We have no reasonable explanation for this result for the time being. A better explanation of all these results can probably be given when the dipole moment of PPO is recalculated using the rotational isomeric states theory in the light of the present experimental data.

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