CONFORMATIONAL BEHAVIOUR OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) IN SOLUTION—II

SEDIMENTATION COEFFICIENTS AND PERMEABILITIES IN THE SEMI-DILUTE REGION AS A FUNCTION OF TEMPERATURE

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Abstract—Sedimentation and flotation coefficients of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) solutions have been measured as a function of temperature between 60 and 25°. The solvents were toluene and trichloroethene (TCE). Solvent permeabilities have been calculated from the sedimentation or flotation coefficients. PPO is less permeable to the solvents used than polystyrene of comparable molecular weight is to toluene and cyclohexane. Strong solvation of toluene and TCE by PPO molecules is proposed as an explanation for this finding. The measured permeabilities were used to check an earlier calculation of the change of radius of gyration with temperature from intrinsic viscosity data. A larger decrease in radius of gyration with increasing temperature has been calculated in this way than with the earlier assumption of essentially impermeable polymer coils, i.e. with the assumption of the value 2.5×10^{23} for the universal viscosity parameter Φ_0 .

1. INTRODUCTION

The aim of the present study is to check our earlier estimation [1] of the change of the radius of gyration with temperature for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) dissolved, for example, in toluene. This change was calculated from the change of intrinsic viscosity with temperature, using the Flory–Fox equation:

$$[\eta] = 6^{3/2} \Phi_0 \frac{(R_{gw})_0^3 \alpha_\eta^3}{\bar{M}_w} \quad (\text{for symbols cf. ref. [1]}). \quad (1)$$

We assumed for Φ_0 its “non-draining limit” value 2.5×10^{23} (cgs) [2], regardless of temperature. An objection to this procedure is that Φ_0 has been found to depend on temperature [3]. Another objection is that it has been found that polymers are permeable to solvent (and are *not* “non-draining”) even when the Flory–Fox equation (with Φ_0 for the non-draining limit) gives radii of gyration in accordance with those, determined from light scattering measurements [4].

The reason is that Φ_0 , in cases like these, happens to have the appropriate value, which results in fact from two independent factors, affecting the solvent draining. They are not mentioned as such in the theory underlying the Flory–Fox formula. They are hidden, as it were, in the assumption of (adjustable) friction parameters. Usually, one has to assume large, and physically unrealistic, friction parameters in order to arrive at Φ_0 values which enable us to calculate reasonable radii of gyration when using the Flory–Fox equation.

The first factor that affects solvent draining is the radius of gyration: the larger it is, the higher the permeability of the polymer coil to solvent. The second

factor is “intramolecular clustering”. This concept stems from the representation of polymer coils as clouds of averaged dimension, shape and composition. The clouds are assumed to be composed of clusters of fluctuating volume, the clusters consisting of segments, or of a segment and one or more solvent molecules.

Thus, Mijnlief and Jaspers [5] studied poly- α -methylstyrene in cyclohexane (bad solvent) and in toluene (good solvent). They calculated solvent permeabilities from sedimentation coefficients, measured in a “plug-flow”, or “semi-dilute”, region (i.e. at a concentration where the polymer molecules overlap (see below)). A dramatic increase in permeability with decreasing temperature was found for the bad solvent system: near θ the permeability was twice that at 70–125°. No such effect was found for the same polymer in toluene.

Mijnlief and Jaspers attributed the increase in permeability with decreasing T to an intramolecular rearrangement, consisting of local associations of segments, or groups of segments. This should cause a coarser distribution of polymer material, and thus a higher permeability. They suggested solvent molecule binding to polymer segments as an explanation for the low permeability of poly- α -methylstyrene in toluene (i.e. low with respect to the coils dissolved in cyclohexane). They found the large difference in permeability for the two solvents to diminish with increasing temperature, where specific interactions lose their influence and where clustering of segments starts again (i.e. near the lower critical solution temperature).

The parameter Φ_0 , then, depends in a complicated way on solvent quality, and nothing can be said a

priori about its temperature dependence. Therefore it would be interesting to recalculate the radii of gyration derived previously without the assumption of a constant (non-draining) value of 2.5×10^{23} for Φ_0 .

2. THEORY

The Mijnlief-Wiegel theory of intrinsic viscosity [4] takes the effect of permeability on the intrinsic viscosity directly into account. The permeability K , which appears in their final formula, has to be read from an experimental curve like that given in Fig. 3, at a concentration c defined by:

$$c \equiv \frac{\bar{M}_w}{N_{av}} (\frac{2}{3} \pi R_{gw}^2)^{-3/2}. \quad (2)$$

(The use of weight-averages in this formula is introduced by us; for a justification see below.)

The concentration dependent permeabilities k (Fig. 3) are calculated from sedimentation coefficients s :

$$k = \frac{\eta_0 s}{c(1 - \bar{v}\rho_0)} \quad (3)$$

where

- η_0 = viscosity of solvent
- c = concentration
- $\bar{v}$ = partial specific volume of polymer
- ρ_0 = density of solvent.

(For flotation experiments, the s and the $1 - \bar{v}\rho_0$ are negative, and a positive k is calculated, as it should be.)

Thus, the permeability is taken into account as an experimentally accessible parameter:

$$[\eta] = \frac{4}{3} \pi \frac{N_{av}}{\bar{M}_w} \alpha \Phi(\alpha) Q^{-3/2} \quad (4)$$

where

- $\alpha \equiv K^{-1} Q^{-1}$
- $\Phi(\alpha)$ = function of α (cf. Fig. 2 of [4])
- $Q = 3/(2 R_{gw}^2)$

Just as in our preceding paper, we may calculate C_∞ from R_{gw} , but R_{gw} is derived now from Eqn (4). The best way to calculate R_{gw} from this equation would be an iterative procedure: assume a value for R_{gw} , calculate c [Eqn (2)], read K from Fig. 3 at this c , calculate Q and $\alpha\Phi(\alpha)$, and finally $[\eta]$; repeat these calculations until the best $[\eta]$ is calculated back. We will not follow this procedure, as there are several objections to Eqn (4).

Firstly, the weak point of the Mijnlief-Wiegel theory is the choice of K as the permeability, read from the k - c curve at the concentration defined by Eqn (2). They discuss fully the arbitrariness of this choice in their paper, and suggest a theoretically better procedure (not elaborated as yet). The main consequence of this choice is that the $[\eta]$, calculated from a measured R_{gw} and an experimental k - c curve, always is somewhat higher than the experimental $[\eta]$.

Secondly, the K should be read from a k - c curve in a region where at the same concentration the K values do not depend on polymer molecular weight. This region (the "semi-dilute" region) is characterised by a scaling law behaviour [6]:

$$s \sim c^{-a}. \quad (5)$$

In this region, $\log |s|$ should plot linearly with $\log c$. Thus, we should read K from a k - c curve at a concentration, defined by Eqn (2), in this linear region. As will be seen in Section 4.1, we cannot be sure that our low molecular

weight PPO samples allow us to determine K values which are independent of molecular weight.

Thirdly, the use of weight-averages in Eqn (2) is doubtful. Strictly speaking c should be defined with number averages. As in a given weight of polymer, most molecules have molecular weights in the vicinity of $\bar{M}_w$, we considered Eqn (2) to be an adequate representation for the desired concentration—a weight concentration—of a polydisperse polymer. If c is defined with number-averages, its numerical value is about 30% higher than the c of Eqn (2).

Thus, in view of these objections to a strict application of Eqn (2), which would be necessary for an iterative procedure, we followed another procedure. We introduced two extreme assumptions about the change of R_{gw} with temperature. The first assumption was that R_{gw} remained constant from 60 to 25°, the second, that R_{gw} for 25 and 35° was 10% higher than R_{gw} for 45 and 60°. We adopted values for R_{gw} compatible with experimentally determined values (Table 1), and calculated the consequences of the two assumptions for the change of $[\eta]$ with temperature.

3. EXPERIMENTAL

3.1 Polymers and solutions

Table 1 summarizes some properties of the polymers studied; characterization methods have been given [1]. The polystyrenes were prepared by suspension polymerization (cf. ref. [12] in our preceding paper [1]). Information about solvents and solutions, and the method of approaching the desired temperatures has been given [1].

3.2 Properties of solvents and solutions (Table 3)

Solvent viscosities were determined in two Ubbelohde viscometers, calibrated at the desired temperatures with de-aerated, distilled water. Solvent and solution densities were determined in a PAAR Digital Density Meter (DMA 50, Anton Paar K.G., Graz), calibrated with de-aerated, distilled water and with dry air. The buoyancy factors ($1 - \bar{v}\rho_0$) were determined by plotting solution densities against concentration (in g/ml); the slope is $(1 - \bar{v}\rho_0)$.

3.3 Sedimentation

Sedimentation runs were carried out in a Beckman Model E analytical ultracentrifuge equipped with a temperature-regulating unit and a Schlieren phase plate. 1.5-mm cells were applied for concentrations higher than 1.5 g/100 ml, and 12-mm cells for solutions of lower concentration. The solutions had concentrations under and above c_{full} [cf. Eqn (6)], as indicated in Figs 1–3. Measurements were made at a rotor speed of 64,000 rpm with PPO and with the polystyrenes of lower molecular weight (comparable to PPO), and at a speed of 52,000 rpm for the higher molecular weight polystyrene. Schlieren boundary curves were registered photographically. The peak positions were read from the photographic plates with a reproducibility of 0.01 mm by means of a measuring microscope.

The first photograph was taken as soon as a Schlieren peak was fully visible. The other photographs were taken at time intervals of 8 or 16 min. The experiment was stopped when the last photograph was taken, just over the middle of the cell (mostly after 64 min).

Sedimentation coefficients (or flotation coefficients for the system PPO-TCE) were derived as the slope of the best straight line through the data points $\ln x^*$ (or $\ln x'$) and $2\omega^2 t$, where $x^* = (r^*/r_m)^2$, $x' = (r^*/r_b)^2$, ω = angular speed in radians per second and t = time in sec; r^* = distance of the top of the Schlieren peak to the centre of rotation R , r_m = distance of the meniscus to R , and r_b = distance of the bottom to R .

In this way, pressure dependent sedimentation and flotation coefficients, both denoted by s , were obtained. The rise

Table 1. Symbols and characterization data* of polymers, studied in this work. Temperature 25°, except for cyclohexane (35°)

Polymer†	$\bar{M}_w \times 10^{-4}$	$\bar{M}_z \times 10^{-4}$	Solvent‡	$[\eta]$ (ml/g)	R_{gz} (Å)
PPO-8	6.6 ± 0.3	9.2 ± 0.3	TCE	65.1	160 ± 30
			Tol	64.6	140 ± 20
PPO-9	8.7 ± 0.3	10.4 ± 0.2	TCE	77.9	180 ± 30
			Tol	77.5	160 ± 20
PS-1	11.8 ± 0.5	14.1 ± 0.3	CH	28.7	180 ± 20
			Tol	49.5	—
PS-2	185.0 ± 10.0	—	Tol	356.0	590 ± 40

* Molecular weights ($\bar{M}_w$, $\bar{M}_z$), intrinsic viscosity ($[\eta]$), root-mean-square radius of gyration (z-average, R_{gz}).

† PPO: poly(2,6-dimethyl-1,4-phenylene oxide); PS: polystyrene.

‡ TCE: trichloroethene; Tol: toluene; CH: cyclohexane.

in pressure in the ultracentrifuge cell (from 1 atm. at the meniscus) causes the sedimentation process to slow down when the sedimentation boundary reaches the cell's bottom. The reverse is true for flotation (like PPO in TCE): the sedimentation process is accelerated when the boundary reaches the meniscus. Hence, corrections are needed to obtain "true" sedimentation coefficients, i.e. corrected to the pressure at the meniscus. Unfortunately, for flotation the pressure correction is not as easy as it is for sedimentation (cf. the Appendix).

As we were not able to obtain true sedimentation coefficients for PPO in TCE, we decided to present all s -values in Fig. 1 without pressure correction. Fortunately this enables us to compare our results with those of others [5, 7, 9], who also did not apply pressure corrections. As a rough estimation of the consequences of the pressure effect, we may add 5% to the sedimentation coefficients of the polystyrenes and of PPO in toluene, and 20% to those of PPO in TCE (cf. the Appendix).

4. RESULTS

4.1 Determination of the semi-dilute region

As already stated, for our purpose sedimentation coefficients should be determined in the semi-dilute region. It is not easy to define where the semi-dilute region begins, because the definitely dilute region gradually crosses over to the semi-dilute.

The scaling law behaviour, characteristic for the semi-dilute region, can be established relatively easily for high molecular weight polymers ($\bar{M}_w$ of the order 10^6). As already mentioned [1], we were not able to obtain samples of such high molecular weights for PPO. Hence, we compared the results of sedimentation measurements on solutions of PPO to those on solutions of two polystyrenes. The first of the two polystyrene samples had a molecular weight distribution comparable to that of the PPO; the other one had a high molecular weight, of the order 10^6 (cf. Table 1).

From Fig. 1 the conclusion may be drawn that PPO concentrations higher than the value given by c^* are in the semi-dilute region, where a scaling law applies with coefficients $a = 0.92$ (for PPO in TCE) and $a = 0.84$ (for PPO in toluene). For polystyrene in cyclohexane we find $a = 0.68$ – 0.76 ; in toluene $a = 0.72$; Pouyet and Dayantis [7] found $a = 0.82 \pm 0.03$ for polystyrene dissolved in bromo-

benzene and for poly(methyl methacrylate) dissolved in benzene. Destor and Rondelez [8] found $a = 0.59 \pm 0.03$ for polystyrene in benzene. The data points are too scattered however for an unambiguous establishment of the scaling law behaviour with exponent a belonging to it.

The concentration c^* , where for PPO the semi-dilute region should approximately begin, is within experimental error (in R_{gw}) equal to:

$$c_{full} = \frac{\bar{M}_w}{N_{av}} \cdot \frac{1}{(\frac{4}{3})\pi R_{gw}^3} \quad (6)$$

This concentration c_{full} may be considered as the concentration where the polymer coils begin to interpenetrate, and where the whole solution volume is occupied by the polymer coils. Thus, above c_{full} (or c^*) the solvent mainly flows through the polymer coils during the sedimentation process, and not mainly around

Fig. 1. Scaling law plot for the concentration dependence of sedimentation or flotation coefficients ($|s|$) at 25°. The departure from linearity near c^* corresponds to the gradual onset of the semidilute region where $\log |s|$ is a linear function of $\log c$. Δ PPO-9 in TCE; $\square$ PPO-9 in toluene; $\circ$ PS-1 in toluene; ∇ PS-1 in cyclohexane at 35°; $\bullet$ PS-2 in toluene; $\blacksquare$ PS-2 in cyclohexane at 35°.

Fig. 2. Reciprocal sedimentation coefficient as a function of concentration at 25°. Symbols as in Fig. 1.

them, as it does in the dilute region. Hence, the semi-dilute region is sometimes called the (porous) plug-flow region. As the concentration, defined in Eqn [2], is higher than c_{full} , and as c_{full} is approximately equal to c^* , we assume that it is justified to calculate $[\eta]$ from permeabilities K read from k - c curves in the region above c^* .

4.2 Concentration dependence in the dilute region

From Fig. 2 we can calculate the concentration dependence parameter k_s for the dilute region ($c < c^*$). This parameter is defined by:

$$1/s(1, c) = (1/s_0)(1 + k_s c) \quad (7)$$

where $s(1, c)$ is the concentration dependent sedimentation (flotation) coefficient corrected for the pressure effect. The s_0 in (7) is corrected both for pressure and

concentration. The s values, plotted in Fig. 2, are however not corrected for pressure (cf. Section 3.3).

The dimensionless friction parameter $k_s/[\eta]$ should, according to the theories of Yamakawa and of Puyn and Fixman, vary between about 0.2 for coiled polymers in a bad solvent to about 1.6 for coiled polymers in a good solvent [2]. Experimentally, for flexible coils values of 1.6 have been found [2]. The $k_s/[\eta]$ values determined by us (corrected for pressure or not) are within experimental error in the expected range, see Table 2. (The slight differences between the k_s values corrected for pressure, and the uncorrected values, are explained in the Appendix.)

For good solvents it has been found especially for $\bar{M}_w > 5 \times 10^5$ that above c^* the plots $1/s(1, c)$ vs c deviate downwards from the linear behaviour below c^* , while for bad solvents the deviation is upwards [5]. This is not what we have found: all plots begin to deviate upwards above c^* . The reason might be that we studied compounds with lower molecular weights than those reported in other studies, and/or that we plotted in Fig. 2 reciprocal sedimentation coefficients uncorrected for pressure.

4.3 Permeability k as a function of concentration and temperature

From the sedimentation coefficients, not corrected for the pressure effect, permeabilities k have been calculated according to Eqn (3). The values used for the constants η_0 , $\bar{v}$ and ρ_0 in this formula, are presented in Table 3.

An example of the dependence of k on concentration c at 25° is given in Fig. 3. The permeability of our low molecular weight polystyrene in toluene agrees, in the plug-flow region, rather well with those determined by Nyström and Roots [9]. They are of the same order of magnitude as those of the poly(α -methyl styrene) samples studied by Mijnlief and Jaspers [5]. This gives confidence in our determinations of permeabilities for such low molecular weight polymers as our PPO samples. See also the points in Fig. 3 for our polystyrene of $\bar{M}_w 1.85 \times 10^6$. The permeabilities of a lower molecular weight PPO (PPO-8; see Table 1) were measured in toluene and TCE at 25° only. The results coincided over the whole range with the curve drawn for PPO-9 in Fig. 3.

For our low molecular weight polystyrene dissolved in cyclohexane, we found (see Fig. 4) at temperatures above θ the same increase in permeability with decreasing temperature as found for higher mol-

Table 2. Concentration dependence coefficient* for sedimentation in the dilute region

Polymer	Solvent	$k_s/[\eta]$	$k_s/[\eta]$
		(no pressure correction)	(pressure correction applied)
PPO-9	TCE	1.43†	1.50†
	Tol	1.29	1.34
PS-1	Tol	1.60	1.60
	CH	0.70	0.70

* Reproducibility of the presented figures 10–15%.

† Flotation coefficient.

Table 3. Solvent and solute properties, necessary for the calculation of permeabilities according to Eqn (4)

Solute	Solvent	T (°C)	η_0^* (cP)	$\rho_0^\dagger$ (g/ml)	$\bar{v}_1^\ddagger$ (ml/g)	$1 - \bar{v}_1\rho_0$
PPO-9	TCE	25	0.538	1.4543	0.85	-0.243
		35	0.495	1.4374	0.87	-0.247
		45	0.452	1.4210	0.88	-0.253
		60	0.406	1.3964	0.90	-0.257
	Tol	25	0.550	0.8628	0.85	0.270
		35	0.493	0.8533	0.84	0.282
		45	0.441	0.8437	0.83	0.300
		60	0.383	0.8389	0.83	0.303
PS-1	Tol	25	0.550	0.8628	0.91	0.209
		35	0.493	0.8533	0.89	0.240
	CH	35	0.755	0.7629	0.93	0.290

* Solvent viscosity.

† Solvent density.

‡ Partial specific volume of polymer.

ecular weight polymers in θ -solvents by Mijnlief and Jaspers [5], and later by Nystrom and Roots [9].

In toluene as well as in TCE the permeability of the PPO molecules practically does not change with temperature. An example of the variation (or rather the constancy) of k with temperature at concentrations in

Fig. 3. Permeability k [Eqn (3)] as a function of concentration at 25°. Symbols as in Fig. 1.

the plug-flow region is given in Fig. 4 and in Table 4, together (for comparison) with permeabilities of other polymer molecules at the same concentration. We note that for the PPO concentration of Fig. 4 demixing (i.e. crystallization) in toluene starts at 15°.

The increase in permeability with decreasing temperature, as we seem to have found for polystyrene in toluene, is probably not significant: we should take an experimental uncertainty in k of about 7% into account (resulting from errors of 5% in s , 2% in $1 - \bar{v}_1\rho_0$, and 1% in η_0 and c). Moreover, Mijnlief and Jaspers [5] did not find such an increase in permeability with decreasing temperature for the comparable system poly(α -methylstyrene) in toluene.

The apparent differences in permeability of the PPO molecules in TCE and toluene disappear when we take this uncertainty and the pressure correction (a systematic error, see Section 3.3) into account. The differences in permeability between PPO molecules and polystyrene molecules of comparable molecular weight are significant, however.

For other concentrations in the plug-flow region (cf. also Table 5) the picture remains the same: for PPO no significant increase in permeability with descending temperature, but a definite difference in permeability between PPO and polystyrene, not to be ascribed to accidental or systematic errors.

4.4 Change of R_{gw} and C_∞ with temperature, calculated from earlier measurements of $[\eta]$

Starting from the assumptions mentioned above (Section 2), we recalculated R_{gw} and C_∞ as a function of temperature from $[\eta]$ as a function of temperature. The results are represented in Tables 5 and 6: in Table 5 the calculation of $[\eta]$ for a polystyrene sample is given for comparison. We see that the Mijnlief-Wiegel theory [4] describes $[\eta]$ rather well in terms of measured permeabilities. The agreement may be improved by the use of permeabilities roughly corrected (cf. Section 3.3) for the pressure effect (Table 5).

Our first assumption, R_{gw} constant with temperature, turned out to be unrealistic: it predicted a continuous rise in $[\eta]$ with temperature (Table 5). The

Table 4. Permeabilities at $c = 3.0$ (g/100 ml) (in the porous plug flow region), as a function of temperature. (No pressure corrections applied)

Polymer	Solvent	Experiment	Permeability $k \times 10^{13}$ (cm ²)			
			$T = 25^\circ$	$T = 35^\circ$	$T = 45^\circ$	$T = 60^\circ$
PPO-9	TCE	This work	0.37	0.37	0.35	0.35
	Tol	This work	0.52	0.49	0.48	0.49
PS-1	Tol	This work	1.01	0.89		
PS	Tol	Ref. [9]*	0.8			
P α MS	Tol	Ref. [5]†	1.22			
PS	Dec	Ref. [9]	5.0		1.7	
PS-1	CH	This work		2.14		
P α MS	CH	Ref. [5]		3.26		

* Polystyrene, $\bar{M}_w$ 3.9×10^5 ; solvents toluene and decaline. Data derived from Nyström and Roots [9], Fig. 3 of their paper.

† Poly- α -methylstyrene $\bar{M}_w$ 6.5×10^6 ; solvents toluene and cyclohexane. Data derived from Mijnlief and Jaspers [5], Table 1 of their paper.

second assumption, a 10% change in R_{gw} , was more realistic (Table 6).

Values for C_x , calculated from the second assumption, are represented in Table 7. They are compatible with the K_θ -values, determined earlier [1], although the K_θ values calculated from the 5th column of Table 7 are somewhat too high with respect to those measured from our Stockmayer–Fixman plots [1].

Their percentage change with temperature, however, remains within the experimental errors of the earlier determined K_θ . The slight discrepancy between calculated and observed K_θ -values is not interesting (it must be attributed to our rather arbitrary choice of some R_{gw} values compatible with the experimentally determined ones, given in Table 1); the agreement between a calculated and an observed change in K_θ is the point of interest here. The change, calculated by applying the Mijnlief–Wiegel theory, turns out to be larger than that by applying the Flory–Fox theory [1]; cf. Table 7.

DISCUSSION

From the course of the permeability k with concentration c as represented in Figs 3 and 4, we may conclude that in the semi-dilute region the PPO molecules in toluene as well as in TCE are less permeable to solvent than the polystyrene molecules are in toluene or in cyclohexane. We attribute this difference to strong solvation of solvent molecules to PPO segments.

There are several indications for such a strong binding of solvent molecules. Firstly, it has been observed [10] that for solid PPO no crystalline X-ray pattern is obtained, unless a certain amount of solvent is present. It has been shown experimentally [10] that solvent molecules fitted well into the polymer backbone helices from which the crystalline parts are composed. Secondly, measurements of adiabatic compressibility of PPO solutions in toluene could be interpreted consistently by assuming binding of solvent molecules to PPO segments [11]. Thirdly, our preliminary measurements of heats of solution of PPO in toluene and TCE showed that the PPO solutions were highly non-athermal: we found large negative χ_{HT} -values, of the order -1.0 .

Assuming that the solvent binding over the studied temperature range does not vary appreciably, we can explain a second finding concerning PPO molecules viz. their temperature independent permeability.

This phenomenon does *not* mean that the universal viscosity parameter Φ_0 should be independent of temperature. A change in radius of gyration changes the permeability of the PPO molecule [according to Eqn (2) and Fig. 3] and hence the Φ_0 value for the system in question. This is in our opinion more realistic than the assumption of $\Phi_0 = \text{constant} = 2.5 \times 10^{23}$ (the non-draining limit value). Hence, we think that we have found more support for the conclusion of our preceding paper viz. the conformational transition of dissolved PPO molecules between 45 and 35°, i.e. a change in unperturbed dimensions [$(R_{gw})_0$, or C_r].

In our preceding paper, we found such a change in unperturbed dimensions to be rather small. Moreover, this change was calculated assuming a constant expansion factor α_η of 1.1. A decrease in α_η with

Fig. 4. Permeability k [Eqn (3)] as a function of temperature. Concentration constant for each curve. All concentrations between 2 and 3 g/ml, i.e. above c^* of the polymer. Symbols as in Fig. 1.

Table 5. Calculation of intrinsic viscosity $[\eta]$ [according to Eqn (4)] from measured permeabilities, assuming no change in radius of gyration (weight-average, R_{gw})

Polymer	Solvent	T (°C)	R_{gw} (Å)	c (g/ml)	K (cm ²)	K' (cm ²)	$[\eta]_{calc}$ (ml/g)	$[\eta]_{calc}'$ (ml/g)	$[\eta]_{exp}$ (ml/g)
PPO-9	TCE	25	150	0.0141	1.39	1.67	138	121	77.9
		35	150	0.0141	1.39	1.67	138	121	76.5
		45	150	0.0141	1.32	1.58	144	126	74.1
		60	150	0.0141	1.22	1.46	154	133	73.5
PPO-9	Tol	25	133	0.0204	1.00	1.05	104	100	77.5
		35	133	0.0204	0.98	1.03	104	102	76.0
		45	133	0.0204	0.92	0.97	112	107	73.0
		60	133	0.0204	0.91	0.96	112	108	72.0
PS-1	CH	35	150	0.0188	4.56	4.79	39.0	37.0	28.7

Column 4: approximated by $R_{gw} = (\bar{M}_w/\bar{M}_z)R_{gz}$.

Column 5: cf. Eqn (2).

Column 6: Permeability $k \times 10^{13}$, belonging to c of column 5; taken from curves like Fig. 3.

Column 7: same K , corrected for pressure effect.

Column 8: $[\eta]$ calculated from K .

Column 9: $[\eta]$ calculated from K' .

increasing temperature might have resulted in a constant $(R_{gw})_0$, or C_x , i.e. in no conformational transition. Such a decrease in α_H would not be unexpected, viz. the negative χ_H . The decrease in R_{gw} , assumed in Table 6, would result in a decrease in $(R_{gw})_0$ or C_x with temperature, even with a decrease in α_H over the same temperature range, provided that α_H changes by less than 10%. We can assume that this is the case, as we found α_H to remain in the range 1.1–1.2 [1]. This,

and the larger decrease in R_{gw} with increasing temperature calculated by the Mijnlief-Wiegel theory, supports our earlier conclusion concerning the conformational change of PPO.

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Table 6. Calculation of the temperature dependence of $[\eta]$ from Eqn (4), based on an assumed 10% change in R_{gw} . (Column headings of Table 5; polymer: PPO-9)

Solvent	T (°C)	R_{gw} (Å)	c (g/ml)	K' (cm ²)	$[\eta]_{calc}$ (ml/g)	$[\eta]_{exp}$ (ml/g)
TCE	25	150	0.0141	1.67	121	77.9
	35	150	0.0141	1.67	121	76.5
	45	135	0.0195	0.92	119	74.1
	60	135	0.0195	0.85	127	73.5
Tol	25	133	0.0204	1.05	100	77.5
	35	133	0.0204	1.03	102	76.0
	45	120	0.0276	0.58	100	73.0
	60	120	0.0276	0.60	97	72.0

Table 7. Estimation of change in C_x of PPO with temperature. Estimations derived from the dependence of intrinsic viscosity on temperature, interpreted according to the Mijnlief-Wiegel theory [Eqn (6)] and the Flory-Fox theory [1]

Solvent	T (°C)	$[\eta]_{exp}$ (ml/g)	Mijnlief-Wiegel		Flory-Fox	
			R_{gw} (Å)	C_x	R_{gw} (Å)	C_x
TCE	25	77.9	150	5.4	129	4.0
	35	76.5	150	5.4	128	3.9
	45	74.1	135	4.4	127	3.9
	60	73.5	135	4.4	126	3.8
Tol	25	77.5	133	4.2	129	4.0
	35	76.0	133	4.2	128	3.9
	45	73.0	120	3.5	126	3.8
	60	72.0	120	3.5	125	3.7

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APPENDIX

For sedimentation, a sedimentation coefficient corrected to $p = 1$ (atmosphere) (i.e. the pressure at the meniscus) is most easily achieved by calculation of the coefficients of a cubic polynomial through the data points $\ln x^*$ and $2\omega^2 t$ [12]:

$$\ln x^* = \frac{s_0}{1 + \alpha} 2\omega^2 t - (s_0)^2 \times \frac{(2\alpha + 1)m - \alpha}{2(\alpha + 1)^3} (2\omega^2 t)^2 + O\{(2\omega^2 t)^3\} \quad (\text{A.1})$$

where $\alpha \equiv k_s c$ and m = pressure effect parameter.

(We have omitted the third power term because it is rather clumsy: it is however not negligible.)

The calculation of the first coefficient of the above expansion can be simulated graphically, by drawing the initial tangent to the curve through the data points $\ln x^*$ plotted vs $2\omega^2 t$. The slope of this tangent is $s(1, c) = s_0/(1 + k_s c)$.

The application of this procedure to the data points of a flotation run (with $\ln x'$ instead of $\ln x^*$; for the notation see Section 3.3) would lead to an entirely wrong result. We have shown elsewhere [13] that for the flotation case the first coefficient of an expression analogous to (A.1) should read:

$$\frac{s_0}{(1 + \alpha/h)} \cdot \frac{h}{q} \quad (\text{A.2})$$

where

$$\begin{aligned} q &= (r_h/r_m)^2 \\ h &= q/(1 - m + mq) \\ m &= \text{pressure effect parameter [12].} \end{aligned}$$

A correction of the uncorrected flotation coefficients (denoted in the text by s , and obtained in the way described in Section 3.3) was estimated as follows. For the lowest concentration we assumed α to be zero, and from the first and the second coefficient of a cubic expansion [like (A.1)] for $\ln x'$ vs $2\omega^2 t$, we then calculated m to be in the range 0.5–1.1. Now q and h being known, we calculated s_0 values for the other concentrations from the first coefficients of the expansions for $\ln x'$ against $2\omega^2 t$. The uncorrected flotation coefficients s all turned out to be about 20% lower than the corresponding values of s_0 obtained as just described. (The flotation analogue to the expansion (A.1) has been given [13].)

Calculation of k_s from the plot of the reciprocal initial slopes (A.2) was not successful [13]. The large experimental uncertainty in m , and the poor reproducibility of the initial tangent slopes, prevented a satisfactory determination of k_s for the floating system PPO–TCE. For some temperatures, the values of k_s thus obtained were higher than the values of k_s obtained from the uncorrected s , for other temperatures they were lower.

From the values of the initial tangent slopes $s(1, c)$ for the sedimenting systems, compared to the values for s (obtained as described in Section 3.3), we concluded the $s(1, c)$ to be about 5% higher than the uncorrected s . The k_s , obtained from $s(1, c)$ or from s , practically did not differ.