

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

INTRINSIC VISCOSITY AS A FUNCTION OF TEMPERATURE

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Abstract—Intrinsic viscosities $[\eta]$ of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) solutions have been measured as a function of temperature between 60 and 25°C. The solvents were toluene and trichloroethene. In both solvents, the $[\eta]$ - T curve exhibited a point of inflection in the range 45–35°. This phenomenon is explained as a conformational transition, which is possibly involved in the nucleation process of the solution crystallization of PPO. Assuming constancy of the coil expansion factor α_i and the solvent draining over the whole temperature interval, a slight increase of characteristic parameter C_∞ with decreasing temperature has been calculated.

INTRODUCTION

Dilute solutions (say <5–10%) of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in toluene show phase separation phenomena upon cooling to appropriate temperatures. According to Koenhen *et al.* [1, 2] these phenomena may be interpreted consistently as crystallization phenomena. Turska and Janeczek [3] found that PPO may also crystallize from decalin. Data of Broens *et al.* [4] suggest that trichloroethene (TCE) should be “better” than toluene as a solvent for PPO: solutions of PPO in TCE must be cooled to much lower temperatures than solutions in toluene in order to obtain phase separation. An alternative way to obtain crystallization is to add a *n*-alcohol to the PPO–TCE mixtures [4].

Koenhen *et al.* [2] performed kinetic studies on self-seeded and on homogenous crystallizations of PPO from dilute toluene solutions. They inferred that the crystallization process should involve a nucleation process in two steps, the first being a conformational transition, the second nucleation and growth of crystallites.

In this paper we report the results of measurements concerning the supposed first step of the nucleation process, viz. the conformational transition. We chose as experimental methods light scattering and viscometry as a function of temperature (25–60°C), as many conformational transitions have been detected in this way [5–9]. As already stated, PPO does not crystallize as readily from TCE as from toluene. The conformational transition, supposed to be related to the incipience of nucleation, should therefore occur in TCE solutions in a lower temperature region than in toluene solutions.

Our study differs from earlier studies [10, 11] on the conformation of PPO; the main difference is that we measured at temperatures in the vicinity of the melting point curve of the PPO–toluene system (cf. Ref. [1], Fig. 6) in the dilute region, whereas others

did not study the temperature dependence of conformation [10], or measured only at 25 and 90°C [11].

These earlier studies showed PPO molecules to be random coils, with unperturbed dimensions close to those of a freely rotating chain. In this respect, they may be said to exhibit “flexibility”. This “dimensional” or “equilibrium” flexibility should be clearly distinguished however from the “kinetic” (or “dynamic”) flexibility, which for PPO is rather low. Thus, PPO molecules will be referred to as “tightly coiled” (cf. Akers *et al.* [11]), or “random coils with low chain mobility”, or “stiff coils”.

EXPERIMENTAL

Polymer samples

We prepared several samples of PPO according to the recipe of McCaffery [12]. The highest mol wt sample had \bar{M}_n 33,000, \bar{M}_w 58,000 and \bar{M}_z 96,000. Fractionations according to published procedures [10, 11] were unsuccessful, giving only small yields, with \bar{M}_w never above 100,000. Hence we adopted the following procedure.

100 g of PPO freshly prepared was dissolved in 1 l. of boiling toluene. The solution was cooled and kept for 24 hr at 27°C in a thermostat. (During this time the solution was constantly stirred.) The stirrer was then stopped, to allow the crystallized PPO to settle for another 24 hr. The slurry containing finely divided PPO was filtered on a glass filter No. 4 and dried *in vacuo* at 80°C. The dried product was redissolved to give a 10% solution in chloroform and precipitated by dripping the solution with stirring in a five-fold excess of methanol. The voluminous flocculate was filtered through a Buchner funnel, washed several times with methanol and dried as above.

As a result of this procedure, we obtained from every synthesized PPO sample one fraction of a slightly higher \bar{M}_w . Thus, from 100 g of the highest mol wt sample we were able to synthesize (see above), we obtained 15 g of the fraction called PPO-9 in Table 1.

Solvents and solutions

Toluene (analytical grade, Merck) and TCE (stabilized, Baker Chemicals) were used without further purification.

Table 1. Intrinsic viscosities $[\eta]$ of PPO samples as a function of molecular weight and polydispersity. Temperature 25°C

PPO*	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{M}_z/\bar{M}_w	$[\eta]$ (ml/g) Toluene	$[\eta]$ (ml/g) Trichloroethene
1	8000†	1.6†	1.4†	—	16.2‡
2	25,000	1.6	1.4	34.2‡	34.6
3	37,000	1.3	1.4	47.8	48.2
4	39,000	1.9	1.7	48.0	45.0
5	40,000	1.4	1.4	52.8	53.1
6	57,000	1.4	1.4	66.6	67.9
7	63,000	1.4	1.5	70.1	70.5
8	66,000	1.7	1.4	64.6	65.1
9	87,000	1.9	1.2	77.5	77.9

* Poly(2,6-dimethyl-1,4-phenylene oxide).

† Reproducibility of mol wts 3–5%.

‡ Reproducibility of intrinsic viscosities 0.3–0.6 (ml/g).

Solutions of the desired concentrations were prepared and stored at room temperature as well as at 60°C. Measurements at various temperatures were performed by heating as well as by cooling the solutions to the desired temperature.

Light scattering measurements

We performed light scattering measurements at 4–5 concentrations below 1.5% (w/v) and at 3 concentrations above 1.5% in a Fica 50 light scattering photometer, using vertically polarized light of wavelength 546 nm. This wavelength is too high for the radii of gyration (R_{gz}) we expected; R_{gz} should exceed $\lambda'/20$ (where λ' is the wavelength in the solution.) In our case R_{gz} just was of the order of $\lambda'/20$. We had to resort to this wavelength because our solutions always had a brownish colour (high mol wt were even strongly coloured) and absorbed light at 436 and 365 nm.

Reproducible determinations of \bar{M}_w , second virial coefficient and radius of gyration were more easily achieved for the toluene solutions than for the TCE solutions. The best results for the latter were obtained for solutions clarified by filtering through Fluoropore 0.2 μ filters (of Millipore Corp.); for the toluene solutions, the conventional Millipore 0.22 μ could be used. Light scattering measurements were performed at 11 angles between 30 and 150° to the incident beam. For the calibration constants and an example of a light scattering plot, see Koehen and Smolders [1].

Refractive index increments were measured on a Brice Phoenix refractometer. We obtained dn/dc values at 25, 35, 40 and 60° of 0.116, 0.128, 0.133 and 0.136 for toluene solutions, and 0.139, 0.145, 0.152 and 0.160 for TCE solutions.

Viscometry

A capillary viscometer of the Ubbelohde suspended-meniscus type, with efflux time of 135 sec for toluene and 60 sec for TCE at 25°C, was used. For the determination at higher temperatures, the viscometer was closed with a silicon-rubber stopper between the measurements to reduce evaporation of the solvent. Relative viscosities η_r were calculated directly as t/t_0 , t being the efflux time for the solution and t_0 that for the solvent. We determined η_r for 2 series of measurements per PPO-sample or per temperature, each series consisting of 5–6 concentrations in the range $(1-10) \times 10^{-3}$ g/ml.

For each series, $(\ln \eta_r)/c$ and $(\eta_r - 1)/c$ were plotted against concentration c . Always straight lines were obtained, with regression coefficients better than -0.96 and 0.99, respectively. The intrinsic viscosity $[\eta]$ was calcu-

lated as the mean value of the intercepts. In spite of the good correlation, the slopes of the Huggins plot [13] $(\eta_r - 1)/c$ vs c did not reproduce very well: Huggins' coefficients k_H in the range 0.42–0.49 were calculated (for both solvents).

The values of $[\eta]$, presented in the tables and in the graph, are the mean values, obtained in the way just described for the 2 series of measurements per temperature or per PPO-sample.

Osmometry

A Hallikainen Model 1361 automatic osmometer was used with gel cellophane membranes (Sartorius membrane filter SM 11539). Measurements at 5 concentrations below 1.5% were carried out in toluene as a solvent.

Gel-permeation chromatography

A Waters gel-permeation chromatograph was used with a series arrangement of four columns ($\frac{3}{8}$ in. \times 4 ft each) packed with styragels of porosity ratings 10^5 , $3 \cdot 10^4$, 10^3 and 250 Å. Tetrahydrofuran was used as solvent with a column temperature of 30°C. The flow rate was 1 ml/min. A differential refractometer with a flowing reference cell was used as detector. The columns were calibrated with PPO-samples of known \bar{M}_n - and \bar{M}_w -values, previously determined by osmometry and light scattering. An empirical peak-broadening correction was applied, based on GPC measurements on polystyrenes for which \bar{M}_n , \bar{M}_w and \bar{M}_z were known (osmometry, light scattering, equilibrium distribution in the ultracentrifuge (cf. Ref. [14]).

RESULTS

Characteristic parameters of PPO

Our PPO samples generally had lower mol wts than those studied earlier [10, 11]. Our intrinsic viscosities were 5–15 units higher than those of others [10, 11] for comparable mol wts. We ascribe this to differences in polydispersity between the samples. In order to take polydispersity into account, we inserted values of \bar{M}_w in all the formulae, mentioned in this paper.

We determined for all samples by means of a least squares analysis the parameters K_w and a of the equation

$$[\eta] = K_w \bar{M}_w^a \quad (1)$$

and found for toluene at 25°C

$$K_w = (3.1 \pm 0.2) \times 10^{-3} \text{ and } a = 0.70 \pm 0.01$$

and for TCE at 25°C

$$K_w = (3.3 \pm 0.2) \times 10^{-3} \text{ and } a = 0.70 \pm 0.01.$$

These values differ slightly from those previously published [10, 11]. This may be ascribed not only to differences in polydispersity, but also to the smaller molecular weight region studied by us.

From the Stockmayer-Fixman equation, as modified by Yamakawa [15].

$$[\eta]/\bar{M}_w^{0.5} = K_\theta + 0.346\phi_0 B \bar{M}_w^{0.5} \quad (2)$$

we calculated, with the data for all our PPO samples, the unperturbed dimension parameter K_θ and the solvent-solute interaction ("excluded volume") parameter B . For ϕ_0 we used the value 2.5×10^{23} [15]. For toluene we found $K_\theta = 0.170 \pm 0.010$ and $B = (2.2 \pm 0.4) \times 10^{-27}$ and for TCE $K_\theta = 0.155 \pm 0.015$ and $B = (2.5 \pm 1.0) \times 10^{-27}$. These values again differ slightly from those of other workers [10, 11] for comparable solvents.

The above values for K_θ and B were calculated (by means of least-squares analyses) for 25°C. Unfortunately, the points were too scattered to enable us to find a trend in K_θ and/or B with raising temperature: all K_θ and B values, determined at higher temperatures were within experimental error equal to those at 25°C.

From the K_θ we calculated $[\eta]_\theta$ and from $[\eta]_\theta$ and $[\eta]$ we calculated expansion factors α_η [15]. We found α_η in the range 1.1–1.2, in good agreement with earlier values [10, 11]. All the values of α_η at all temperatures were found to be in this range. Thus, α_η for PPO is not only small as compared to other coil polymers [11] but also is nearly independent of temperature.

Our value of α_η gives an excluded volume parameter z according to [15]:

$$\alpha_\eta^3 = 1 + 1.05z \quad (3)$$

in the range 0.3–0.7. The interpenetration factor ψ , defined by [15]:

$$A_2 = 4\pi^{1.5} N_{Av} (R_{gw}^3 / \bar{M}_w^2) \psi \quad (4)$$

and calculated from the data of Table 2 (with R_{gw} approximated by

$$R_{gw} = ((\bar{M}_w / \bar{M}_z) \cdot R_{gz})$$

is for PPO in TCE and toluene in the range 0.17–0.30. The agreement with other values of ψ , experimentally determined or theoretically derived (cf. [15]), is not good: a ψ value of 0.30 is out of range, even for $z = 0.7$. This might mean that the averaged values for A_2 given in Table 2 are too high. This supposition is confirmed by the calculation of the dimensionless parameters $A_2 \bar{M}_w / [\eta]$: they are also too high (1.2–1.5), as they are expected to be 1.0–1.2 [15].

The values of the radii of gyration were, at all temperatures, in the ranges given in Table 2. No definite trend in R_{gz} with rising temperature was found. The poor reproducibility in the determinations of the radius of gyration especially in TCE solutions implied that we were not able to determine reliable solubility (χ -) parameters for the TCE solutions from the same measurements by Scholte's method [16]. This method was applied to the PPO-toluene system by Koenhen *et al.* [1]; within experimental error, we found for this

Table 2. Radius of gyration (z -average) and second virial coefficient A_2 as determined from light scattering. Temperature 25°C

PPO	\bar{M}_w	Solvent	R_{gz} (Å)	$A_2 \times 10^4$ (mol·ml/g ²)
8	66,000	TCE*	160 ± 30	12 ± 6
		Tol†	140 ± 20	15 ± 3
9	87,000	TCE	180 ± 30	10 ± 2
		Tol	160 ± 20	10 ± 2

* Trichloroethene.

† Toluene.

system the same χ -parameters and the same dependence of χ on concentration as Koenhen *et al.* We confirm their finding that χ is independent of temperature, within experimental error. For PPO-TCE nearly the same values were found for A_2 and R_{gz} as for PPO-toluene; we conclude that the χ -parameters for PPO-TCE do not differ appreciably from those for PPO-toluene, in the dilute solution range. Thus, in this range TCE should not be regarded as a "better" solvent for PPO than toluene.

Intrinsic viscosity as a function of temperature

The results of our viscosity measurements (Fig. 1) indicate a conformational transition. The $[\eta]$ - T curves show a point of inflection in the range 45–35°C; the higher the mol wt, the more pronounced is the effect. Such a dependence on molecular weight for the effects of a conformational transition has been found earlier for other polymers [7].

The intrinsic viscosity depends (a) on the solvent draining (or the permeability) of the macromolecules; (b) on the skeletal geometry; and (c) on the excluded volume (B or z) [the unperturbed dimension parameter K_θ , derived e.g. from Eqn (2), depends on both (a) and (b)]. Hence, determination of the temperature dependence of one of these three parameters from a measured $[\eta]$ - T curve (cf. Ref. [9]) presupposes knowledge (experimental and/or theoretical) concerning the temperature dependence of the other two parameters.

Evans *et al.* [8] showed that a maximum in the $[\eta]$ - T curve, or a steady decrease with increasing T , always means that the temperature coefficient of the unperturbed dimension ($d \ln K_\theta / d T$) is negative, irrespective of the assumptions made about the dependence of $[\eta]$ on α_η and about the dependence of α_η on the excluded volume parameter z . The analysis of Evans *et al.* [8] is based however on the assumption that z increases with increasing T , which means that α_η should not decrease with increasing T .

We found experimentally that the expansion factor α_η is, within experimental error, independent of temperature. We may therefore conclude that, for PPO-TCE and for PPO-toluene, $d \ln K_\theta / d T$ is negative. This confirms the earlier, comparable, conclusion of Akers *et al.* [11] based on Stockmayer-Fixman plots (at 25 and 90°C only, however). Thus, reasoning along the lines pointed out by Evans *et al.* [8], we arrived at a qualitative conclusion about the behaviour of K_θ as a function of temperature; from our Stockmayer-Fixman plots, we could not reach such a conclusion. In

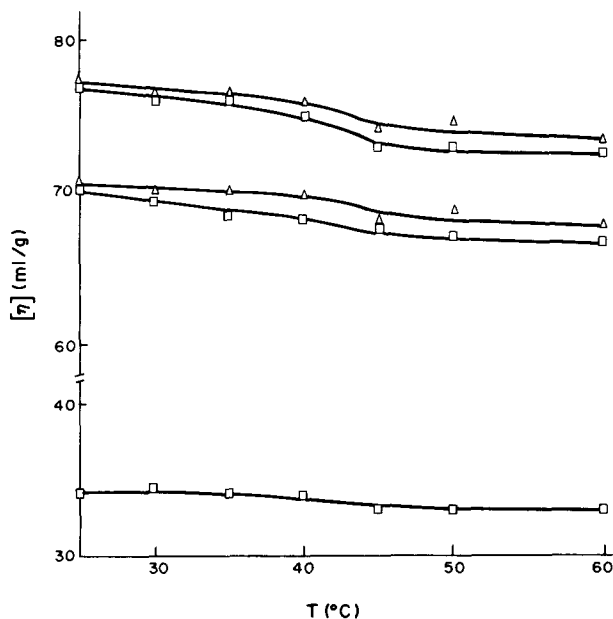


Fig. 1. Intrinsic viscosity as a function of temperature, for PPO samples of three molecular weights. Upper two curves $\bar{M}_w = 87,000$, middle two curves $\bar{M}_w = 63,000$, lowest curve $\bar{M}_w = 25,000$. Δ Solutions in TCE; \square solutions in toluene.

our opinion, the conclusion that $d \ln K_\theta / dT < 0$ holds for the left part of the $[\eta]$ - T curve (i.e. to the left of the point of inflection) as well as for the right part.

Thus, assuming that the permeability is independent of T , we conclude that the peculiar shape of the $[\eta]$ - T curve means that the tightly coiled dissolved PPO molecules adopt a slightly less coiled, somewhat more expanded structure when the solution is lowered in temperature. We believe that the existence of a point of inflection means that this dimensional change is more abrupt than gradual.

The conformational transition occurs in the same temperature region for TCE and toluene. Thus, our hypothesis (that different temperature regions for a conformational transition, if present, should be found) is not confirmed.

Change of characteristic parameter C_∞ with temperature

In order to give a more quantitative interpretation to our measurements of $[\eta]$ at different temperatures, we calculated characteristic ratios C_∞ from the intrinsic viscosities.

The characteristic ratio C_∞ is defined as [17]:

$$C_\infty = \lim_{\bar{N}_w \rightarrow \infty} \frac{6R_{gw}^2/\alpha_s^2}{\bar{N}_w l^2} \approx \frac{6R_{gw}^2/\alpha_\eta^2}{\bar{N}_w l^2} \quad (5)$$

where

- α_s = expansion factor for radius of gyration ($\alpha_s \neq \alpha_\eta$)
- \bar{N}_w = weight-average degree of polymerization (\bar{N}_w is about 700 in our case, and considered to be "large enough")
- l = bond length of repeating unit ($l = 5.4 \text{ \AA}$ [10, 11]).

The ratio C_∞ is related to K_θ by

$$C_\infty = \left(\frac{K_\theta}{\Phi_0} \right)^{2/3} \frac{m}{l^2} \quad (6)$$

where

$$m = \text{molecular weight of repeating unit } (m = 120).$$

The use of the parameter C_∞ has no special advantages over K_θ , except that it has been the subject of numerous theoretical calculations [17] for many types of polymer chains (also as a function of temperature). In order to calculate C_∞ , we first calculated R_{gw} from the measured intrinsic viscosities. To this end we assumed the PPO molecules to be in the non-draining limit. We justify this assumption by referring to the paper of Barrales-Rienda and Pepper [10], who called the PPO molecules "effectively impermeable". (We could confirm their conclusion by calculating permeabilities from sedimentation and flotation coefficients, obtained from experiments with the analytical ultracentrifuge.) For this model, the Flory-Fox formula [15] relates $[\eta]$ to R_{gw} :

$$[\eta] = 6^{3/2} \Phi \frac{(R_{gw})^3}{\bar{M}_w} \quad (7)$$

where

$$\Phi = \Phi_0 (1 - 0.46z). \quad (7a)$$

Another version of the Flory-Fox formula reads [15]:

$$[\eta] = 6^{3/2} \Phi_0 \frac{(R_{gw})_0^3 \alpha_\eta^3}{\bar{M}_w} \quad (8)$$

where $(R_{gw})_0$ = unperturbed radius of gyration, from which C_∞ is calculated as:

$$C_\infty = \frac{6(R_{gw})_0^2}{\bar{N}_w l^2}. \quad (9)$$

Assuming that $\alpha_s = \alpha_\eta = 1.1$, for all four temperatures, we calculated R_{gw} , $(R_{gw})_0$ and C_∞ from Eqns (5) and (9) as shown in Table 3.

Calculation of K_θ from C_∞ by means of Eqn (6) leads to values within experimental error equal to

Table 3. Radius of gyration (weight average) and characteristic ratio C_z as a function of temperature, calculated from intrinsic viscosities by means of the Flory-Fox equation. Molecular weight M_w of PPO: 87,000

Temp. (°C)	Solvent	$[\eta]$ (ml/g)	R_{gw} (Å)	C_z	$(R_{gw})_0$ (Å)	C_z
25	TCE	77.9	129*	4.0†	112‡	3.6§
35	TCE	76.5	128	3.9	111	3.6
45	TCE	74.1	127	3.9	110	3.5
60	TCE	73.5	126	3.8	109	3.5
25	Tol	77.5	129	4.0	111	3.6
35	Tol	76.0	128	3.9	111	3.6
45	Tol	73.0	126	3.8	109	3.5
60	Tol	72.0	125	3.7	109	3.5

* Calculated from Eqn (7) with $z = 0.3$.

† Eqn (5) with $\alpha_s = \alpha_r = 1.1$.

‡ Eqn (8) with $\alpha_r = 1.1$.

§ Eqn (9).

those derived from Stockmayer-Fixman plots. Thus the relative change in C_z with temperature, calculated from the use of the Flory-Fox formula and the assumptions about α_r , is compatible with (though not confirmed by) the results of the Stockmayer-Fixman plots.

DISCUSSION

In toluene as well as in trichloroethene, we found PPO to exhibit a conformational transition in the range 45–35°C, from a tightly coiled structure at temperatures above 45°C to a more expanded form below 35°C. We found no differences between toluene and TCE as to the temperature range where the transition occurs.

For other polymer-solvent systems, dramatic conformational transitions with large changes in $[\eta]$ or in R_{gz} have been found [5–7]. The conformational transition discovered for PPO is of a more modest type. As we gave the solutions sufficient time to reach temperature equilibrium, and as we approached the desired temperatures from above as well as from below, we may consider the conformational transition of PPO to be real, and not to be an artefact caused by kinetic effects.

That the PPO molecules expand when the temperature is lowered can be explained by assuming that in solution those helices are formed which occur in the crystals [3]. We cannot support the explanation by referring to the results of conformational calculations for PPO. As far as we are aware, no such calculations have been carried out. Assuming, however, that the PPO chain in its segment mobility behaves like the poly(oxyethylene) chain (for which calculations of the conformation as a function of helix content and temperature exist [17]), we think that it is justified to say that lowering of temperature increases the number of helical sequences as well as the unperturbed dimensions.

An explanation for the relatively small change in unperturbed dimensions with temperature may be that the potential barriers to rotations or crankshaft movements of (groups of) monomer units are rather

high with respect to RT . They are of the order of 5 kJ for rotations and of 25 kJ for crankshaft movements [18], whereas RT is about 2.5 kJ.

Strictly speaking, we found the conformational transition only for infinitely dilute solutions. The radius of gyration, however, depends on concentration [15]. Thus, we might doubt that a conformational transition (i.e. a change in radius of gyration with temperature) found for infinitely dilute solutions would persist in more concentrated solutions. Theories for dilute solutions [15] (up to 2–3% polymer, in our case), where no extensive overlapping of polymer chains occurs, indicate that the way in which the radii of gyration change with concentration should be the same for each temperature, provided that the excluded volume parameters z and B may be assumed to be independent of temperature.

Assuming this, we may then infer that for dilute PPO solutions (up to 2–3%) the same conformational transition occurs as that found for infinitely dilute systems. Toluene solutions containing 2–3% PPO crystallize in the temperature region 8–20°C. Thus, we may consider as confirmed the hypothesis of Koenhen *et al.* [2] that nucleation and growth of crystallites is preceded by a conformational transition, at least for dilute toluene solutions up to 2–3% PPO.

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