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Unperturbed Chain Dimensions of Polyethyleneterephthalate and Polyethylene 1, 2-Diphenoxyethane *p*, *p'*-Carboxylate

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ABSTRACT: The limiting viscosity number $[\eta]$ and the number-average molecular weight M_n were measured on polyethyleneterephthalate (PET) and polyethylene-1, 2-diphenoxyethane-*p*, *p'*-dicarboxylate (PEPC) fractions in *o*-chlorophenol (OCP) and phenol/tetrachloroethane (P/T, 1/2, W/W) mixture. The following Mark—Houwink—Sakurada relations were established:

for PET $[\eta]=2.97\times10^{-2}M_n^{0.75}$ in OCP at 35°C
$[\eta]=1.09\times10^{-2}M_n^{0.84}$ in P/T at 35°C
for PEPC $[\eta]=1.45\times10^{-1}M_n^{0.59}$ in OCP at 35°C
$[\eta]=1.12\times10^{-1}M_n^{0.63}$ in P/T at 35°C

From these viscosity data as well as literature data the Flory K value (and hence, the conformational parameter σ) was determined, by use of the Kamide, *et al.*, plot and the Stockmayer and Fixman plot, as 0.160 (1.22) for PET and 0.251 (1.35) for PEPC. The large discrepancy in viscosity data of other literature and this study could well be explained in terms of the polydispersity of the polymer samples used. It has been concluded that a PEPC chain is less flexible than a PET chain.

KEY WORDS Unperturbed Chain Dimension / Polyethyleneterephthalate / Polyethylene-1, 2-Diphenoxyethane-*p*, *p'*-Dicarboxylate / Mark—Houwink—Sakurada Equation /

Although polyethyleneterephthalate (polyoxyethyleneoxyterephthaloyl) (usually referred to as PET) is an industrially important polymer as resourse material for synthetic fibers, its solution properties and molecular characteristics have not been extensively disclosed. For example, for PET solutions[1] there is considerable disagreement among reported values of K_m and a of the Mark—Houwink—Sakurada (MHS) equation,

$$[\eta]=K_m M^a \qquad (1)$$

Here $[\eta]$ is the limiting viscosity number, M is the molecular weight, K_m and a are constants. Accordingly, the reliable value of unperturbed chain dimensions has not been settled, as yet. In this paper we attempt to determine the MHS equations for PET solutions in *o*-chlorophenol (OCP) and in a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (P/T) and to evaluate the unperturbed chain dimensions from these limiting viscosity number data. Polyethylene-1, 2-diphenoxyethane-*p*, *p'*-dicarboxylate (polyoxyethylene oxy-carbonyl 1, 4-phenylene oxyethylene oxy-1, 4-phenylene carbonyl, hereafter referred to as PEPC) is a kind of polyester—ether and has a chemical structure closely related to that of

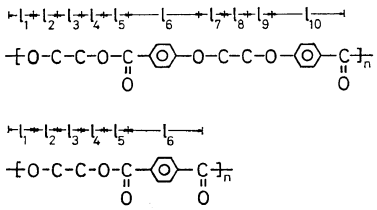

Figure 1. Chemical structure of PEPC as compared with PET.

PET as shown in Figure 1. We evaluate the unperturbed dimension of PEPC also and compared it with that of PET for disclosing the effect of increasing phenolic density in the main chain and the effect of introduction of ether linkage on the chain flexibility.

EXPERIMENTAL

Polymerization

A mixture of 1 mol of dimethylterephthalate and 2 mol of ethyleneglycol was polycondensed in the presence of 0.065 mol of calcium acetate and 0.09 mol of antimonytrioxide into polyethyleneterephthalate (PET). The ester exchange reaction was carried out at 190°C for 2 hr under nitrogen atmosphere and the polycondensation reaction was performed at 280°C for 6 hr under the pressure of 1 mmHg. The limiting viscosity number $[\eta]$ of a whole polymer, thus prepared, in *o*-chlorophenol at 35°C was 82. The viscosity average molecular weight M_v of this polymer was determined as 3.6×10^4 by substituting the $[\eta]$ value into the MHS equation (eq a) established here.

PEPC was prepared from dimethyl 1, 2-diphenoxyethane p, p'-dicarboxylate and ethyleneglycol by using calcium acetate and antimonytrioxide as catalysts under the same condition as those employed in PET. A polymer thus prepared indicated $[\eta]=80$ in a mixture of phenol and tetrachloroethane (P/T, 2/3, W/W) at 35°C and $M_v=3.7\times10^4$, which was obtained from the MHS equation established in this study.

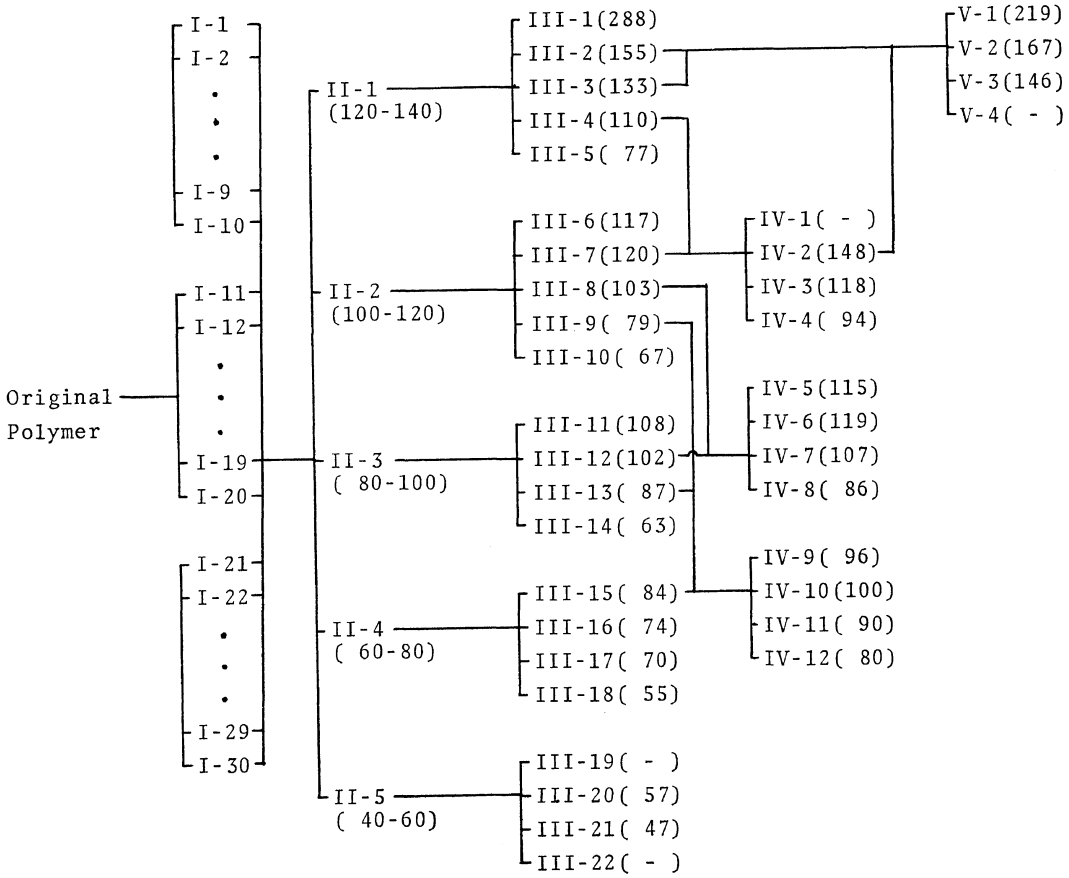

Figure 2. Schematic diagram of the refractionation procedure; numbers in parenthesis denote limiting viscosity number $[\eta]$ in *o*-chlorophenol at 35°C.

Fractionation

Three runs of successive precipitational fractionation (SPF) (solvent, a P/T mixture (2/3, w/w), precipitant, *n*-heptane; initial concentration, 0.3 g/d*l*; temperature, 20°C; total number of fractions per a run, 10) were carried out on PET and PEPC, respectively, and 30 fractions were obtained for each polymer. Among them, five groups were prepared by combining similar fractions whose $[\eta]$ coincide within a range of 20. Each mixture was refractionated separately by dissolution of P/T mixture and subsequent precipitation into 4—5 fractions by SPF in the manner similar to that described above. The above operation was repeated two or three times and finally 18 fractions of PET and 17 fractions of PEPC were obtained. Schematic diagram of this refractionation procedure is demonstrated in Figure 2 in the case of PEPC. The fractions thus prepared are expected to exclude low and high molecular weight components effectively. The determination of the accurate molecular weight distribution of the PET and PEPC fractions is a matter of considerable difficulty and was not attempted here. Among them, nine fractions for each polymer were selected for subsequent use. The theoretical study on the precipitational refractionation procedure employed here for the system of polymer in a single solvent suggests that the ratio of the weight- to number-avarage molecular weight, M_w/M_n, of the fractions thus prepared except for a few initial fractions lies between 1.3 and 1.4, almost independent of M_w. This contrasts sharply with simple successive precipitational fractionation. In addition, to our experience, the quasi-ternary system (polymer/solvent/nonsolvent) produces the fractions having a M_w/M_n approximately 0.1 greater than that obtained for the quasibinary system (polymer/solvent). Therefore, the M_w/M_n of the fractions may be averaged to about 1.5. This expectation was experimentally in part confirmed by measurements of M_w (by the light scattering in trifluoroacetic acid at 30°C) and of M_n (by the membrane osmometry in *o*-chlorophenol at 45°C) on several fractions. In this case, an increase in M_w/M_n by combination of the polymer fractions of similar $[\eta]$ is equally cancelled by a decrease in M_w/M_n by repetition of the fractionation.

Membrane Osmometry

Osmotic pressure π was measured at 45°C on a Hewlett-Packard high speed membrane osmometer 502 for PET and PEPC solutions in *o*-chlorophenol. Here, Membrane 08 (produced by Carl Schllicher and Schuell Inc.) was utilized. Membrane was conditioned consecutively by using water, isopropyl alcohol, toluene, and *o*-chlorophenol. M_n was determined from $\lim_{C\to 0} \pi/C$ (C, concentration) by extrapolating the plot of π/C *vs.* C. Meyerhoff and Shimotsuma[3] concluded that M_n, determined by membrane osmometry in *o*-chlorophenol and *m*-cresol, is less reliable because of permeation of low molecular weight components through membrane (Sartorius ultracellafilter allerfeinst grade), which was indirectly deduced from the experimental fact that M_n by membrane osmometry is larger than M_n by end group analysis. In this study, for both PET and PEPC solutions, π value was maintained constant at least several hours and the height of the solvent cup for solvent/solvent combination was not significantly variated. From these it was comfirmed that the permeation of low molecular weight components through membrane does not occur in this study.

Solution Viscosity

Dilute solution viscosity of PET and PEPC solutions in *o*-chlorophenol and in P/T (1/2, w/w) mixture was measured at 35°C by using a Ubbelohde suspension type viscometer having a negligible-small kinetic energy correction term (less than 0.1%). The correction of shear rate dependence of viscosity was not applied. $[\eta]$ was obtained by extrapolation of linear plot of η_{sp}/C against C (Huggins plot, η_{sp} is specific viscosity) to infinite dilution.

RESULTS AND DISCUSSION

Figure 3a and b show the double logarithmic plot of $[\eta]$ and M_n of PET and PEPC in *o*-chlorophenol and a mixture of P/T (1/2, w/w). The following MHS equations were obtained from viscosity data in Figure 3 by the least square method, where $[\eta]$ is expressed in m*l*/g.

$$[\eta]=2.97\times 10^{-2}M_n^{0.75} \quad \text{PET in OCP at 35°C} \tag{a}$$

$[\eta]=1.09\times10^{-2}M_n^{0.84}$

PET in P/T (1/2, w/w) at 35°C (b)

$(1.92\times10^4<M_n<6.15\times10^4$, sample number 9)

$[\eta]=1.45\times10^{-1}M_n^{0.59}$ PEPC in OCP at 35°C (c)

$[\eta]=1.12\times10^{-1}M_n^{0.63}$

PEPC in P/T (1/2, w/w) at 35°C (d)

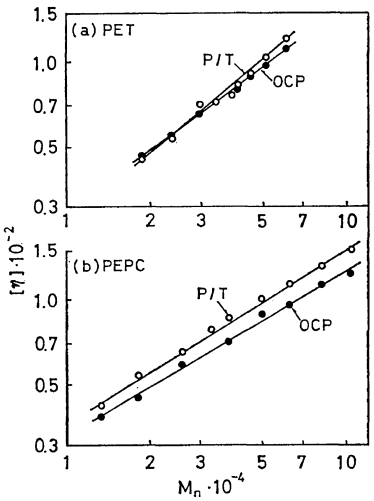

Figure 3. Log—log plot of limiting viscosity number $[\eta]$ *vs.* the number-average molecular weight M_n for polyethyleneterephthalate (PET) and polyethylene-1, 2-diphenoxyethane-*p*, *p'*-dicarboxylate (PEPC) in *o*-chlorophenol (closed mark) and in a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (1/2, w/w) (open mark) at 35°C.

$(1.38\times10^4<M_n<1.065\times10^5$, sample number 9)

The values of K_m and a obtaind in this study, together with representative literature values of K_m and a, which were recalculated by the least square method, from $[\eta]$ and the molecular weight data in literature are tabulated in Table I. In Table I, only data having correlation coefficient between $\log[\eta]$ and $\log M$ larger than 0.98 were adopted. As is evident from Table I, the parameters K_m and a show a large variation. This can, at least in part, be explained by: (1) relatively low confidence of M_n by end group analysis; (2) membrane permeation of low molecular weight component in whole polymers and in fractions with comparatively wide molecular weight distribution; (3) experimental difficulty encountered in solvent purification in the light scattering measurement; and (4) wide variation of the polydispersity of the polymer samples employed, in particular when M_n is used. It will be shown later that the factor (4) plays an important role.

Equation a for PET in OCP is very similar to the corresponding equation recalculated from Meyerhoff—Shimotsuma's data of M_n by the end group analysis (M_n (EG)) (see Table I) and to the original equation determined by them ($[\eta]=3.00\times10^{-2}\ M_n^{0.74}$).[3] This seems to indicate that the polymolecularity of the fractions employed for establishing eq 1 in this study is virtually identical with that of Meyerhoff and Shimotsuma.[3] Meyerhoff and Shimotsuma obtained the molecular weight of the polymer

Table I. Mark—Houwink—Sakurada equations for polyethyleneterephthalate in various solvents

Solvent		Temp, °C	$K_m\times10^2$	a	No. of samples, Fr.	No. of samples, W.P.	Mol·wt range, $M\times10^{-4}$	Method	a*	ref
o-Chlorophenol		25	3.19	0.74	7	—	1.4— 6.7	EG	0.797	3
		25	1.11	0.82	23	—	1.8—10.7	MO	0.785	3
		25	4.34	0.70	7	—	2.3—11.1	SD	0.787	3
		35	2.97	0.75	9	—	1.9— 6.2	MO	0.780	This work
Phenol/ 1, 1, 2, 2-Tetrachloroethane	1/1 (v/v)	20	1.08	0.88	—	7	0.5— 2.0	EG	0.745	4
	〃	20	2.07	0.78	11	—	0.6— 2.3	EG	0.754	4
	〃	20	2.24	0.81	—	9	0.5— 2.5	EG	0.755	5
	3/5 (v/v)	30	5.84	0.65	—	9	2.6—11.8	LS	0.789	6
	1/2 (w/w)	35	1.09	0.84	9	—	1.9— 6.2	MO	0.780	This work
Trifluoroacetic acid		30	5.77	0.66	—	9	2.6—11.8	LS	0.789	6

EG, end group analysis; MO, membrane osmometry; SD, sedimentation-diffusion; LS, light scattering.

samples by three methods; the end group analysis (M_n (EG)), the membrane osmometry (M_n (MO)), and the sedimentation—diffusion method (M_{sd}). M_{sd} lies midway between the weight-average molecular weight M_w and M_n. For the polymers with the Schulz—Zimm distribution (eq 2), M_{sd} is given by[8]

$$M_{sd}=M_w\{1-(1+a)/3(1+h)\}$$
$$=M_n(1+h^{-1})\{1-(1+a)/3(1+h)\} \quad (2)$$

with

$$h^{-1}=(M_w/M_n)-1 \quad (3)$$

The averaged value of the ratio M_{sd}/M_n is estimated as 1.22 for six samples used by Meyerhoff—Shimotsuma and a is 0.70 (see Table I). Putting these values into eq 2, h and hence, M_w/M_n were estimated as 2.29 and 1.44, respectively. That is, $M_{sd}=0.83\ M_w$.

In this manner, the polydispersity of the polymer fraction used by Meyerhoff and Shimotsuma was evaluated. With use of $M_w/M_n=1.44$ thus obtained, the MHS equations of Meyerhoff and Shimotsuma in *o*-chlorophenol (Table I) were transformed into those for the monodisperse polymers, where the molecular weight distribution of the polymer fractions used here approximated with the Schulz—Zimm distribution.

$$[\eta]=2.50\times10^{-2}M^{0.74} \quad \text{by } M_n \text{ (EG)} \quad (e)$$

and

$$[\eta]=3.93\times10^{-2}M^{0.70} \quad \text{by } M_{sd} \quad (f)$$

Here, the effect of the polydispersity on the relations between $[\eta]$ and M_{sd} was assumed to be identical with that on the relation of $[\eta]$ and M_w. This assumption introduced an error not greater than a few % in K_m value in eq f.

The MHS equation for the monodisperse PET in *o*-chlorophenol can also be calculated by putting $a=0.75$ and $h=2.00$ as:

$$[\eta]=2.26\times10^{-2}M^{0.75}$$
$$\text{PET in } o\text{-chlorophenol at } 35°\text{C} \quad (a)'$$

In deriving eq a′, the Schulz—Zimm distribution was assumed for the polymer fractions. However, this assumption introduces an innegligible effect on K_m. For example, 2.25×10^{-2} was obtained in place of 2.26×10^{-2} in the case when the log-normal distribution was assumed.

Although the parameters K_m and a in eq f are somewhat different from those in eq a′, the almost identical value of M_v can be evaluated from eq e, f, and a′ for a given value of $[\eta]$. Therefore, we can conclude that both eq e and f are practically indistinguishable from eq a′.

The composition of a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (1/2, w/w, ≃43/57, v/v at 35°C) used in this study is fairly near to that (1/1 v/v at 20°C) in the study of Griehl and Neue.[4] In fact, eq b for PET in a P/T mixture is analogous to the corresponding equation recalculated from Griehl and Neue's data as shown in Table I. If the difference in measuring temperature is taken into account, the consistency between the two equations is much more improved. Equation b was converted, according to the procedure described above, into

$$[\eta]=0.838\times10^{-2}M^{0.84} \quad (b)'$$

which holds for the monodisperse polymer samples.

Using the viscosity data of $[\eta]$ in a P/T mixture (1/3.5, v/v≃(1/2.4 w/w) at 20°C, M_w and M_w/M_n in the paper of Wallach (Table I of ref 6), we calculated the MHS equation for monodisperse PET in P/T mixture as follows:

$$[\eta]=0.896\times10^{-2}M^{0.84} \quad (g)$$

where the two highest molecular weight frations in the Wallach's paper were discarded for establishing eq g, because as Figure 2 in ref 6 illustrates, data points of these polymer samples deviate largely from the straight line (shown Figure 4) drawn to pass through the other data points. Obviously, eq g is in an excellent agreement with eq b′ obtained here. The slight difference in the composition of P/T in mixtures between our study and Wallach's study (P/T; 1/2, w/w, and 1/2.4, w/w) brings a very small effect on $[\eta]$. Meyerhoff and Shimotsuma observed the difference in the parameters between the MHS equations in *o*-chlorophenol obtained by them with use of M_{sd} and that converted by them from the original MHS equation in P/T mixture of Wallach (M_w) and they concluded that this kind of difference may be due to some systematic difference between M_{sd} anh M_w. The data of Wallach in P/T mixture can be, however, interpreted well in terms of the polydispersity

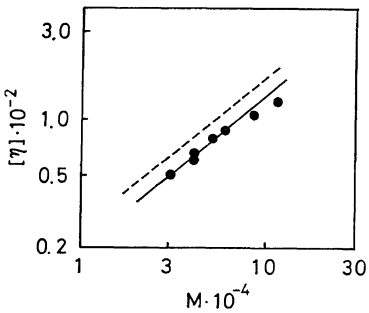

Figure 4. Log—log plot of intrinsic viscosity $[\eta]$ in a phenol/1, 1, 2, 2-tetrachloroethane mixture and the molecular weight M for molecularly uniform PET samples: Straight line, the MHS equation obtained in this paper (see, eq b′); closed mark, data of Wallach in which the polydispersity effect on $[\eta]$ were corrected for each sample by using M_w/M_n data in Table I of ref 6, broken line eq b.

of the samples used if we take into account of eq 2.

If $M_w/M_n=1.9$ and 2.1 are assumed for the whole polymers employed in Griehl—Neue and Conix's equations (Table I), these equations can be reduced to eq b′ provided that the polydispersity effect is properly corrected. The values assumed here are very reasonable from the standpoint of the polymerization mechanism of PET.

The molecularly polydispersity of PEPC fractions is expected to be of the same order of magnitude as that of PET fractions, because almost the same operating conditions of the fractionation was employed. The MHS equations of the monodisperse PEPC are obtained from eq c and d as

$$[\eta]=0.128M^{0.59} \quad \text{PEPC in OCP} \qquad (c)'$$

and

$$[\eta]=0.098M^{0.63} \quad \text{PEPC in P/T mixture} \qquad (d)'$$

Unfortunately the Flory's theta solvents have not yet been found for PET and PEPC. The unperturbed chain dimensions (UCD) of these polymers were then evaluated from measurements of dilute solution properties, including $[\eta]$, M_n, and the MHS equation, carried out in good solvents (*o*-chlorophenol and a mixture of phenol and 1, 1, 2, 2-tetrachloroethane). For this purpose, the two widely accepted methods, *i.e.*, the Kamide, *et al.* (FF—Fi) method[9,11] and the Stockmayer—Fixman method[12] were utilized.

From the combination of the Flory—Fox intrinsic viscosity equation;

$$[\eta]=KM^{1/2}\alpha_\eta^{\ 3} \qquad (4)$$

and the Fixman's expression for excluded volume effect;

$$a=2z+1 \qquad (5)$$

Kamide and Moore[9,10] derived the relation:

$$-\log K_m+\log[1+2\{(a-0.5)^{-1}-2\}^{-1}] = -\log K+(a-0.5)\log M_0 \qquad (6)$$

and from the same combination Stockmayer and Fixman obtaind;

$$[\eta]=KM^{1/2}+0.5\,\Phi_0BM \qquad (7)$$

with

$$K=\Phi_0(\bar{r}_0^{\ 2}/M)^{3/2} \qquad (8)$$

$$\alpha_\eta^{\ 3}=[\eta]/[\eta]_\theta \qquad (9)$$

$$\alpha=(\bar{r}^2)^{1/2}/(\bar{r}_0^{\ 2})^{1/2} \qquad (10)$$

$$z=(3/2\pi)^{3/2}B(\bar{r}_0/M)^{-3/2}M^{1/2} \qquad (11)$$

Φ_0 represents the Flory viscosity constant at theta solvent, whose theoretical value is $2.87\cdot10^{23}$ for $[\eta]$ in m*l*/g when the draining effect is absolutely ignorable, $\bar{r}^2$ and $\bar{r}_0^{\ 2}$ are the mean square end to end distance of the chain in nonideal and ideal solvents, respectively, $[\eta]_\theta$ is limiting viscosity number in theta solvent, B is the long-range interaction parameter between polymer and solvent, M_0 a parameter depending on the molecular weight range, $M_1\sim M_2$, to which eq 1 applies.

In the case when the draining effect in negligible, the geometric mean, $(M_1M_2)^{1/2}$, can be regarded as M_0. Thus a graph of $-\log K_m+\log[1+2\{(a-0.5)^{-1}-2\}^{-1}]$ *vs.* $(a-0.5)\log M_0$ (Kamide, *et al.* (FF—Fi) plot) or a graph of $[\eta]/M^{1/2}$ as a function of $M^{1/2}$ (Stockmayer—Fixman plot) enables us to evaluate $-\log K$ or K from the intercept.

The PET and PEPC data are graphed according to eq 6 and 7 as shown in Figures 5 and 6. In Figure 5 are included the literature data points, in which the exponent a in eq 1 is smaller than the upper limit of the applicability of eq 6, a^*,

$$a^*=1-1/\log M_0 \qquad (12)$$

In the ninth column of Table I the value of a^* calculated according to eq 12 is given for comparison. The slight difference in the slope of the Kamide, *et al.* (FF—Fi) plot for PET reflects the difference of the molecular weight range, in which eq 1 holds. By inspection of Figure 5 the unperturbed chain dimensions of both PET and PEPC are not significantly influenced by the solvent nature (*o*-chlorophenol and a mixture of P/T) and the contribution of the draining effect to $[\eta]$ can be materially ignored. The values of K determined from the intercept of the both plots are summerized in Table II. $K=$ 0.202 and 0.309 were determined on average from the Kamide, *et al.* (FF—Fi) plot for PET and PEPC, respectively. The K value, obtained from the Stockmayer—Fixman plot for PET, varies depending on the solvent nature and from authors to authors.

The Stockmayer and Fixman's extrapolation method appears not to reliable for PET in a

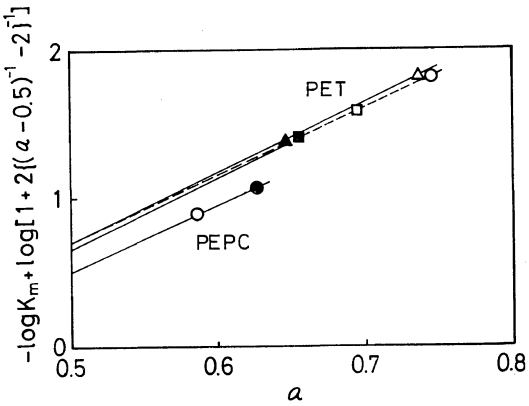

Figure 5. The plots of Kamide, *et al.* (FF—Fi) for polyethyleneterephthalate (PET) and polyethylene-1, 2-diphenoxyethane-*p*, *p'*-dicarboxylate (PEPC): ○, *o*-chlorophenol (this study); △, *o*-chlorophenol (Meyerhoff—Shimotsuma, M_n (EG)); □, *o*-chlorophenol (Meyerhoff—Shimotsuma, M_{sd}); ●, a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (1/2, w/w) (this study); ▲, a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (1/1, v/v) (Wallach, M_w); ■, trifluoroacetic acid (Wallach, M_w).

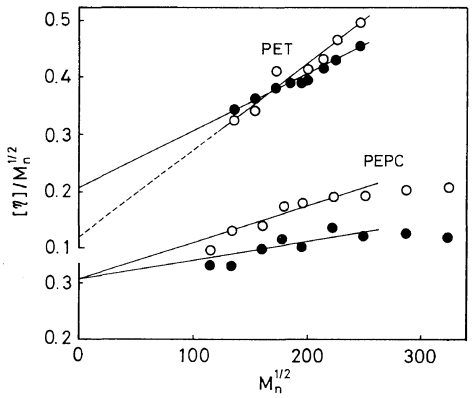

Figure 6. The Stockmayer and Fixman plot for polyethyleneterephthalate (PET) and polyethylene-1, 2-diphenoxyethane-*p*, *p'*-dicarboxylate (PEPC) in *o*-chlorophenol (closed mark) and in a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (1/2, w/w) (open mark).

Table II. Estimation of Flory K value and unperturbed chain dimensions of PET and PEPC

Polymer		PET						PEPC	
Solvent		OCP[a]			P/T[b]		TFA[c]	OCP[a]	P/T[b]
Original data		This work	MS(M_n(EG))[d]	MS(M_{sd})[e]	This work	W[f]	W[f]	This work	This work
$K.10$	by Kamide plot	1.96	1.96	1.95	—	2.08 (1.66)[g]	2.17 (2.11)[g]	3.09	3.09
	by SF polt	2.06	(2.0)[h]	(2.1)[h]	1.2	(2.55)[i]	(2.28)[i]	3.09	3.09
σ	by Kamide plot	1.30	1.30	1.30	—	1.28 1.23	1.30 1.34	1.44	1.44
	by SF plot	1.33	1.31	1.33	1.11	1.42	1.37	1.44	1.44

[a] *o*-chlorophenol; [b] phenol/1, 1, 2, 2-tetrachloroethane; [c] trifluoroacetic acid; [d] Meyerhoff and Shimotsuma (M_n (EG) was used);[3] [e] Meyerhoff and Shimotsuma (M_{sd} was used);[3] [f] Wallach;[6] [g] estimated by Kamide, *et al.*; [h] estimated by Meyerhoff and Shimotsuma;[3] [i] caluculated by us from the values of $(\bar{r}_0^2/M)^{1/2}$ and Φ in literature (see, Table 3 and footnote in page 24 of ref 6).

P/T mixture as is the case for the Kamide, *et al.* plot, because this polymer/solvent system is apparently outside of the applicable limit of the Stockmayer—Fixman plot ($a^*=0.78<a=0.84$) and the unusually small intercepted value (0.120) was obtained. K was averaged to 0.211 from the Stockmayer—Fixman plot on data obtained in this study and literature available except for PET in a P/T mixture. In good solvents, the extrapolated value of the plot at $M^{1/2}=0$ has a tendency to be much lower than the true value of K, as first pointed out by Kamide and Moore.[10] The straight lines drawn through the two sets of points of the Stockmayer and Fixman plot for PEPC have a common intercept, leading to a single value of K (0.309) independent of solvent.

In summary, the following values are determined for K at 35°C:

$$K=0.202 \quad \text{for PET} \qquad (\text{h})$$

and

$$K=0.309 \quad \text{for PEPC} \qquad (\text{i})$$

Thus, the value of K is about 50% greater for PEPC than it is for PET.

It should be born in mind that the K value estimated by using eq 6 and 7 may have considerable error, depending on the polymolecularity of the fraction, particularly if M_n is employed. Therefore, strictly speaking the K value for the monodisperse polymer samples should be determined if one wishes to correlate UCD, accordingly the conformational parameter with the chemical structure of the macromolecules. The K value for the molecularly uniform polymer samples was determined from viscosity data obtaind here and those in the Meyerhoff and Shimotsuma's paper, in which we can estimate the polymolecularity of the samples. Figure 7 shows the Kamide, *et al.* (FF—Fi) plot for PET and PEPC, which were calculated from eq a′—d′ and e—g. For PET/*o*-chlorophenol system K was found to be 0.160 and for PEPC/*o*-chlorophenol and P/T mixture systems $K=0.251$ was obtaind. Figure 8 shows the Stockmayer—Fixman plot for PET, which were obtained from $[\eta]$ and M_w values, calucu-lated from M_n (OS), M_n (EG) and M_{sd} by putting $M_w/M_n=1.5$. The data points of this paper and of Meyerhoff and Shimotsuma's paper approximate to a single straight line with an intercept at $M_w^{1/2}=0$ of 0.155. This value was corrected for the monodispersed polymer sample as $0.155/0.959=0.160$, where $M_w/M_n=1.5$ was taken for the samples. Finaly, K corresponding to the monodisperse polymer, was given for PET in *o*-chlorophenol as 0.160. In a similar manner, $K=0.251$ (corrected) was evaluated from the Stockmayer—Fixman plot ($[\eta]/M_w^{1/2}$ *vs.* $M_w^{1/2}$) for PEPC. The values corresponding to the monodisperse polymer are considerable smaller than those averaged from Table II. The Stockmayer—Fixman plot for PET/OCP data in this paper and in the study of Meyerhoff and

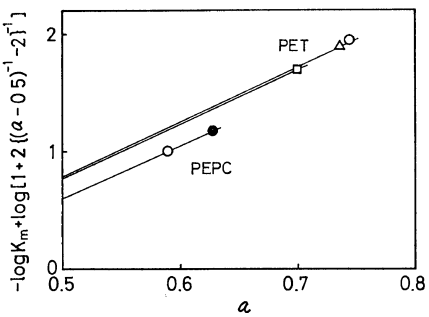

Figure 7. The plote of Kamide, *et al.* (FF—Fi) for polyethyleneterephthalate (PET) and polyethylene-1, 2-disphenoxyethane *p,p′*-carboxylate (PEPC). In this case, the MHS equations corrected for the monodisperse polymer were utilized. The marks have the same meaning as in Figure 5.

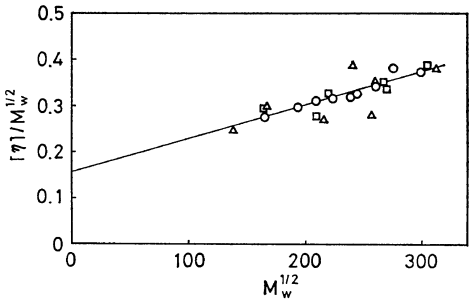

Figure 8. The Stockmayer and Fixman plot for polyethyleneterephthalate (PET) in *o*-chlorophenol: M_w was converted from M_n (OS) (○, this study); M_n (EG) (△, Meyerhoff and Shimotsuma)[3] and M_{sd} (□, Meyerhoff and Shimotsuma)[3] assuming $M_w/M_n=1.5$.

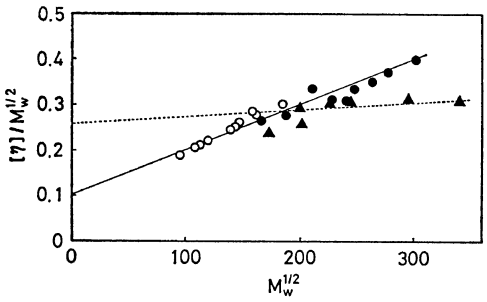

Figure 9. The Stockmayer and Fixman plot for polyethyleneterephthalate (PET) in phenol/1, 1, 2, 2-tetrachloroethane mixture: M_w was calculated from M_n (OS) (●, this study) and M_n (EG) (○, Griehl)[4] assuming $M_w/M_n=1.5$; ▲, Wallach,[6] full line, line drawn in Figure 5 for this system and correct for the polydispersity; dotted line, line drawn by Wallach.

Shimotsuma show $K=0.196$ on the average (Table II) for the original polymer samples and 0.166 for the monodisperse polymers. For PEPC the value of K, evaluated from the Kamide, *et al.* (FF—Fi) plot (0.309) was corrected as 0.261 to the monodisperse polymer, which is not significantly different from that corrected for the polymolecularity after direct evaluation from $[\eta]$ and M_w data. These K values corrected for the polymolecularity are some 20 percent smaller than those uncorrected. Figure 9 shows the data graphed according to eq 7 for PET in P/T mixture. In this figure, the viscosity data of this study together with those of Griehl and Neue (M_n (EG)) and Wallach (M_w) were utilized after conversion of M_n (MO) and M_n (EG) to M_w assuming $M_w/M_n=1.5$. Despite the slight differences in composition of mixtures, the data points, except for the two highest M_w fractions of Wallach, lie to a good approximation, on a straight line over the entire experimentally accessible molecular weight range, cutting the vertical axis of the figure at an ordinate which is equal to $K=0.10$, *i.e.*, the value obtained from Figure 6 and corrected for the polydispersity. However, the K value obtained by this plot (solid line) is underestimated because a mixture of phenol and 1, 1, 2, 2-tetrachloroethane is too good solvent for PET to allow us to estimate the correct K value. It is important to notice that the large difference in data points on $[\eta]$ and M_n or M_w can be well explained in terms of the polymolecularity effect of the polymer samples on $[\eta]$. The dotted line in Figure 9 was drawn by Wallach in his study (see, Figure 4 of ref 6)). As is seen from Figure 9, he overestimated the contributive role of the highest molecular weight data points (sample no. 8 and 9, whose M_w/M_n are 2.63 and 3.14, in Table I of ref 6), which are apparently abnormal, giving a value for K that is in excess of what is expected theoretically. Finally, the Stockmayer and Fixman plot is evidently not applicable to the system of PET and P/T mixture and the K value obtained by this method is susceptible to large error.

The Inagaki, Suzuki, and Kurata relation (eq 13),[16] which has proved to be valid at sufficiently high value (*i.e.*, $\alpha_\eta>1.4$), was then applied to the above polymer/solvent system in question.

$$[\eta]^{4/5}/M^{2/5}=0.786K^{4/5}+0.950K^{4/5}k^{2/3}M^{1/3} \quad (13)$$

where

$$k=0.33B(M/\bar{r}_0^{\,2})^{3/2} \quad (14)$$

Figure 10 shows the data on PET in P/T mixture according to eq 13. The reasonable linearity is observed except the two highest M_w fractions. Here, a straight line was drawn so as to give the K value (0.155) obtained from the Kamide, *et al.* (FF—Fi) plot on monodisperse PET in

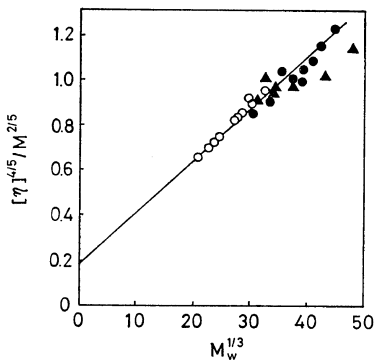

Figure 10. Inagaki, Suzuki, and Kurata plot on polyethyleneterephthalate (PET) in phenol/1, 1, 2, 2-tetrachloroethane mixture. The marks have the same meaning as in Figure 8: Solid line is drawn so as to given the K value (0.155) obtained for PET in *o*-chlorophenol (Figures 6 and 7).

o-chlorophenol (Figure 7) and the Stockmayer and Fixman plot on PET in *o*-chlorophenol (Figure 8) and to pass througth the experimental points. The better fit of the solid line with the experimental data indicates that the Inagaki—Suzuki—Kurata plot is obviously applicable to the PET/P/T system and the K value obtained on PET in *o*-chlorophenol coincides exactly with that on PET in P/T mixture.

Conclusively the K value of both PET and PEPC does not manifest a significant solvent dependence and is determined as 0.160 and 0.251, respectively. In addition, the large difference in viscosity data points found in literature (Griehl,[4] Wallach,[6] and Meyerhoff and Shimotsuma[3]) and in study can be explained in terms of the polydispersity of the polymer samples used.

By assuming $\Phi_0=2.87\cdot10^{23}$, we can calculate $\bar{r}_0{}^2/M)^{1/2}$ from K by use of eq 8. The conformational parameter σ is defined by the relation:

$$\sigma=(\bar{r}_0{}^2/\bar{r}_{0f}^2)^{1/2} \tag{15}$$

where $\bar{r}_{0f}^2$ is the mean-square end to end distance of a hypothetical chain with free internal rotation. Then, σ can be evaluated from the experimentally determined $(\bar{r}_0{}^2/M)^{1/2}$ and the theoretically calculated $(\bar{r}_{0f}^2/M),^{1/2}$ which is 0.675×10^{-8} and 0.709×10^{-8} cm for PET and PEPC, respectively (see Appendix).

The results obtained are listed in Table II. It should be noticed here that σ was recalculated from a literature value of K using the value of $(\bar{r}_{0f}^2/M)^{1/2}$ (0.675×10^{-8} cm). From the apparent values of K which are not corrected with the polymolecularity effect, $\sigma=1.33$ for PET and 1.44 for PEPC were estimated. The former values is in good agreement with that compiled in Polymer Hand Book (2nd ed.).[1] Meyerhoff and Shimotsuma recognized from the systematic comparison of literature data that the most probable value of σ is in the range $1.3\sim1.4$. From the K value for the monodisperse polymer determined above, σ was found to be 1.22 and 1.35 for PET and PEPC, respectively. Although the absolute magnitude of σ varies with the polydispersity of the polymer sample, PEPC is much inferior in its chain flexibility to PET.

The characteristic ratio in the limit for long chains C_∞ is defined by eq 16, where M_b is the mean molecular weight per skeletal bond and l is the mean bond length.

$$C_\infty=(K/\Phi_0)^{2/3}M_b/l^2 \tag{16}$$

$C_\infty=3.5$ for PET and 4.2 for PEPC were determined. The low chain flexibility of PEPC, compared to PET, is confirmed again by adopting C_∞. This suggests that the effect of steric hindrance introduced by increase in phenol group density plays a predominant role as compared with the effect of flexibilization by ether linkage.

APPENDIX

Calculation of $(\bar{r}_{0f}^2/M)^{1/2}$ for PET and PEPC

A repeating unit of PET and PEPC consists of six and ten bonds, of which the bond length is denoted by $l_1, l_2, \ldots$ (see Figure 1). Here, the effective bond length, $\bar{l}$, of a repeating unit can be defined by the relation:

$$\bar{l}^2=\sum_i l_i^2 \tag{A.1}$$

The values of l_i in eq A.1 are given for PET and PEPC as follows:

For PET;

$l_1=l_5=1.34\times10^{-8}$ cm, $l_2=l_4=1.44\times10^{-8}$ cm,
$l_3=1.54\times10^{-8}$ cm, $l_6=5.80\times10^{-8}$ cm

For PEPC;

$l_1=l_5=1.34\times10^{-8}$ cm,
$l_2=l_4=l_7=l_9=1.44\times10^{-8}$ cm,
$l_3=l_8=1.54\times10^{-8}$ cm, $l_6=l_{10}=5.74\times10^{-8}$ cm

For brevity, the valence angle between any two consecutively connected bonds, i and $i+1$, $\theta_{i,i+1}$ is assumed to be identical with each other, that is

$$\theta_{1,2}=\theta_{2,3}=\cdots=\theta_{i,i+1}=\cdots=\bar{\theta}=109.5^\circ \tag{A.2}$$

Then, $(\bar{r}_{0f}^2/M)^{1/2}$ for PET and PEPC chains can be regarded as that of a simply polymeric chain, constituting of effective bonds (molecular weight per bond m) of length $\bar{l}$ and valence angle $\bar{\theta}$. The latter is given by:

$$(\bar{r}_{0f}^2/M)^{1/2}=\{(\bar{l}^2/m)(1-\cos\bar{\theta})/(1+\cos\bar{\theta})\}^{1/2} \tag{A.3}$$

From eq A.1—A.3, we obtain

$$(\bar{r}_{0f}^2/M)^{1/2}=675\times10^{-11}\text{ cm} \quad \text{for PET}$$
$$(\bar{r}_{0f}^2/M)^{1/2}=709\times10^{-11}\text{ cm} \quad \text{for PEPC} \qquad \text{(A.4)}$$

If, all the bonds except for a bond including phenolic (l_6 in PET and l_6 and l_{10} in PEPC) are assumed to have same length (1.54×10^{-8} cm), the approximate values for $(\bar{r}_{0f}/M)^{1/2}$ can be obtained:

$$(\bar{r}_{0f}^2/M)^{1/2}=688\times10^{-11}\text{ cm} \quad \text{for PET}$$
$$(\bar{r}_{0f}^2/M)^{1/2}=719\times10^{-11}\text{ cm} \quad \text{for PEPC} \qquad \text{(A.5)}$$

The value for PET in eq A.5 is very similar to that (687×10^{-11} cm) used by Kurata and Stockmayer (see Table 10 in ref 16) and cited widely in literature. In this paper, in place of eq A.5, eq A.4 was utilized.

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