Characterization of poly(dihalophenylene oxides) in solution

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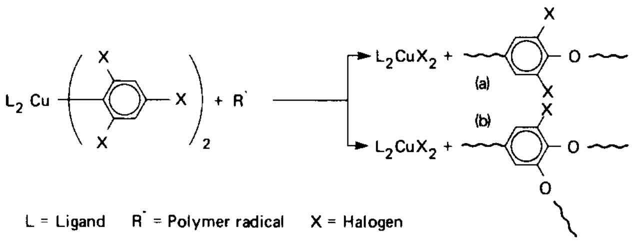
Several different dihalophenylene oxide polymers prepared by thermal decomposition of halophenoxo copper complexes were studied in toluene using light scattering. For polymers of molecular weight around 5×10^4, those obtained from 4-bromo-2,6-dichlorophenoxide, 2-chloro-4,6-dibromophenoxide and 2,4,6-tribromophenoxide appear to be relatively linear with higher values of $\langle S^2 \rangle^{1/2}$, whereas those obtained from 2,4,6-trichlorophenoxide and 2-bromo-4,6-dichlorophenoxide appear to have branched or condensed structures with lower values of $\langle S^2 \rangle^{1/2}$. Values for the intrinsic viscosities and second virial coefficients were measured from ~17 to 50°C for poly(dichlorophenylene oxides) synthesized from 2,4,6-trichlorophenoxide ($M_w = 5.3 \times 10^4$) and from 4-bromo-2,6-dichlorophenoxide ($M_w = 2.49 \times 10^5$). These quantities both pass through a maximum as the temperature increases.

(Keywords: poly(dihalophenylene oxides); light scattering; LCST; UCST; second virial coefficient)

INTRODUCTION

Poly(dihalophenylene oxides) were originally synthesized by Hunter[1] and their synthesis, mechanisms of formation and their structures have subsequently been investigated in several different laboratories[2–11].

It was originally believed that these polymers were highly branched, owing to their seemingly low viscosities[2,6]. Later studies confirmed branching, but indicated that the branches are largely monomeric[8]. When the monomer contained bromine in the 4-position, 1–4 catenation (a) was favoured over *ortho*-substitution (b), leading to a more linear polymer[8].



L = Ligand R· = Polymer radical X = Halogen

The solution properties of these poly(dihalophenylene oxides) have not been previously studied in detail. The present paper reports their detailed characterization by light scattering, differential refractometry, viscometry and differential scanning calorimetry.

EXPERIMENTAL

Materials

Monomers. Halogenated phenols were purchased from Fluka AG, Aldrich or Fisher Chemical as pure analytical grade. Mixed trihalophenols were made by chlorination or bromination of the appropriate dihalophenol. The procedure for halogenation of dihalophenols is now outlined.

Bromination. Dichlorophenols were brominated by mixing two different solutions. Solution (I) was prepared by dissolving 0.1 M bromine with 0.15 M KBr in 150 ml of deionized water. Solution (II) was made by dissolving the required amount of dichlorophenol in a minimum amount of ethanol. Then solution (I) was added to solution (II) dropwise with constant stirring for a given period of time. The precipitated product was cooled on ice for a short time, filtered and dried.

Chlorination. Dibromophenols were chlorinated with sulphuryl chloride. Pure SO_2Cl (15 ml) was added slowly to the required amount of molten sample. The 2,4-dibromophenol reaction mixture was refluxed for 30 min at 150°C and the 2,6-dibromophenol reaction mixture was heated to 50°C for 15 min.

The products were crystallized from pure ethanol. Structures and purities of products were established by ^1H n.m.r. spectroscopy.

Polymers. All the polymers used in present work were prepared according to methods given in the literature[3,7,8]. In each case the monomer was the bis(pyridine) bis(halophenoxide) copper(II) complex. Poly(dihalophenylene oxides) were synthesized from five different chlorinated and/or brominated phenols. A list of these polymers with their specific refractive index increments dn/dc, molecular weights M_w and intrinsic viscosities $[\eta]$ is collected in *Table 1*.

The decomposition solvent for the phenoxo copper complexes was either benzene or toluene at 70°C. The reflux times ranged from 6 to 48 h to give the desired range of molecular weights.

All solvents used were pure analytical grade.

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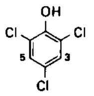
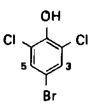
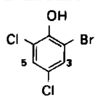
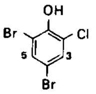
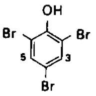
Table 1 Characteristics of different poly(dihalophenylene oxides) synthesized from either chlorinated and/or brominated phenols

Samples*		d*n*/d*c* (ml g^{-1})	$M_w \times 10^{-5}$	[η] (dl g^{-1})
I = 2,4,6-Trichlorophenol (TCP)				
 B1	I_1	0.119	0.47	0.048
	I_2	0.117	0.49	0.052
	I_5	0.119	0.53	0.057
	$I_6{}^a$	0.124	1.14	0.070
II = 4-Bromo-2,6-dichlorophenol (4Br-DCP)				
 B2	II_1	0.122	0.41	0.072
	$II_5{}^b$	0.121	1.74	–
	II_3	0.125	2.49	0.096
	II_8	0.124	4.76	–
III = 2-Bromo-4,6-dichlorophenol (2Br-DCP)				
 B3	III_1	0.118	0.55	0.040
IV = 2-Chloro-4,6-dibromophenol (2Cl-DBrP)				
 B4	IV_1	0.115	0.57	0.047
V = 2,4,6-Tribromophenol (TBrP)				
 B5	V_1	0.111	0.54	0.033

$^a M_w/M_n = 1.44$; $^b M_w/M_n = 1.38$

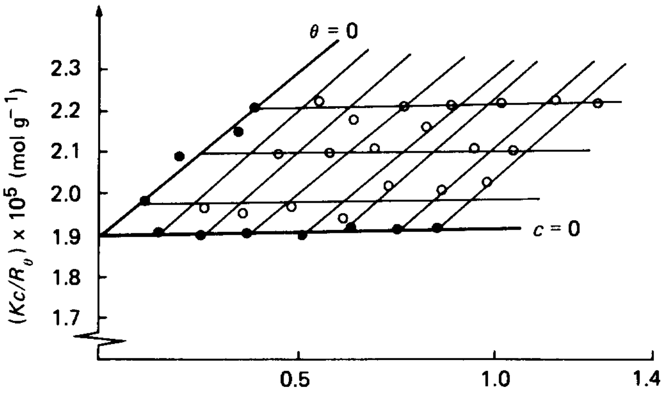


Figure 1 Zimm plot for poly(dichlorophenylene oxide), sample I_5, in toluene at 30°C

Methods

Light scattering measurements were made with a Brice–Phoenix light scattering photometer with unpolarized blue light ($\lambda = 436$ nm). Solutions were directly injected into the cell by filtration through 0.45 μm (type HA) Millipore membrane filters.

The refractive index increments were determined at 30°C and 436 nm wavelength with a Brice–Phoenix differential refractometer model BP-2000 V. The same batch of pure solvent was used for both light scattering and refractive index increment measurements and both instruments were controlled to ± 0.1°C using a circulating water thermostat. The uncertainty in the refractive index increment is ± 0.001 ml g^{-1}.

Intrinsic viscosities were determined in toluene using an Ubbelohde viscometer having an efflux time at 30°C of 250 s. The viscosity of a given solution was measured at several temperatures with the aid of a constant-temperature water bath controlled to ± 0.1°C at the desired temperature.

The glass transition temperatures T_g were measured with either a DuPont-99 series or a Perkin–Elmer differential scanning calorimeter with a scanning rate of 20.00°C min^{-1}.

EXPERIMENTAL RESULTS

Light scattering measurements were performed on all of the samples. Angular measurements from 45° to 135° were carried out in toluene. The typical Zimm plots obtained are shown in *Figures 1* to *4* for samples I_5, I_6, II_3 and II_8. Normal Zimm plots were observed for specific temperatures (*Figures 1* and *3*), but inverted Zimm plots were obtained at higher temperature for these polymers, as seen in *Figures 2* and *4*. However, Zimm plots became badly disturbed at other temperatures which can be due to the polymer associating in solution.

Standard procedures were used to evaluate the light scattering data from Zimm plots as listed in *Table 2* by using a computer program[10].

In the light scattering technique, the temperature dependence of the polymer interaction with solvent can be easily followed by the precise determination of the second virial coefficient A_2 as listed in *Table 3* for samples I_5 and II_3.

For sample I_5, A_2 increased with temperature and passed through a maximum at around 30°C as expected for a system having a θ-point, which is known as the upper critical solution temperature, *UCST* (*Figure 5*). Then A_2 should reach a minimum value below 40°C, which can be taken as a second θ-point, known as the lower critical solution temperature, *LCST*, for this

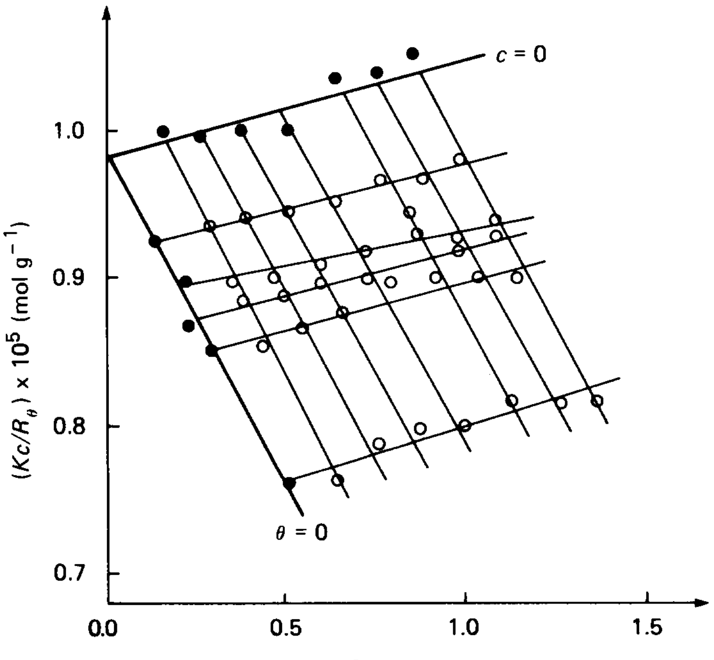


Figure 2 Zimm plot for poly(dichlorophenylene oxide), sample I_6, in toluene at 40°C

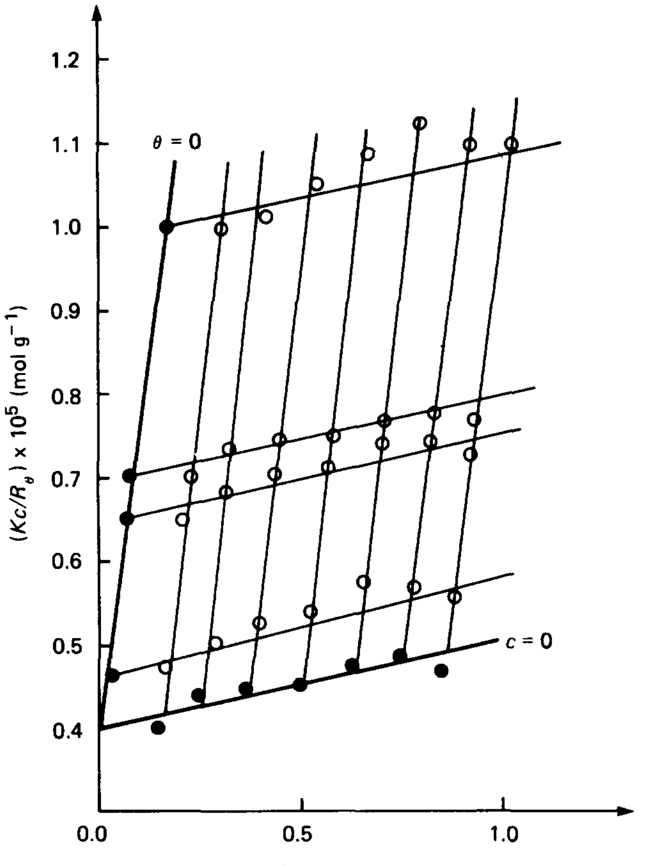


Figure 3 Zimm plot for poly(dichlorophenylene oxide), sample II_3, in toluene at 37°C

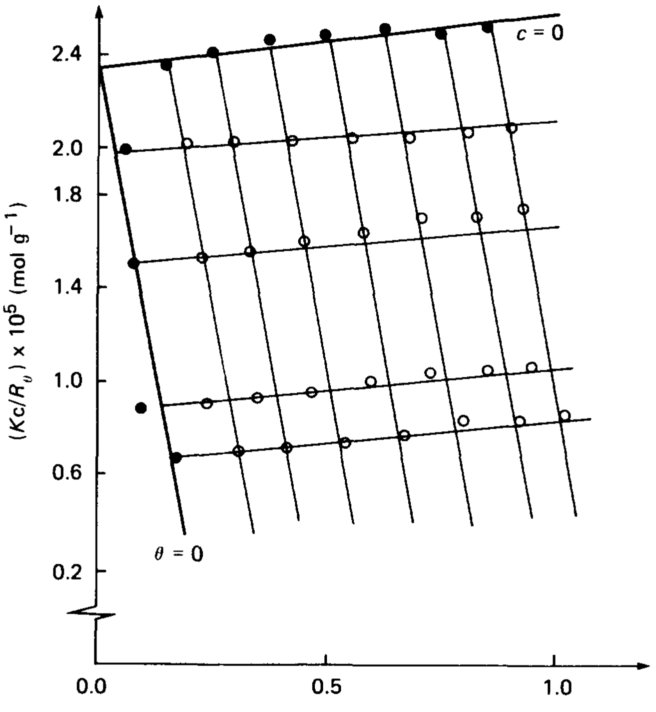


Figure 4 Zimm plot for poly(dichlorophenylene oxide), sample II_8, in toluene at 40°C

system. In agreement with the above system, sample II_3 showed the same behaviour, but it attained its maximum value at around 28°C (*Figure 6*).

The picture presented by $[\eta]$ was similar. The precise determination of $[\eta]$ at the *LCST* and *UCST* was difficult due to its rapid variation with temperature, but the shape

Table 2 Values of the molecular weights, A_2 and $\langle S^2\rangle^{1/2}$ in toluene obtained via light scattering

Samples	$M_w \times 10^{-5}$	A_2 (cm^3 mol g^{-2})	$\langle S^2\rangle^{1/2}$ (Å)	Temp. (°C)
I_1	0.47	−177	129	35
I_2	0.49	4.2×10^{-5}	110	34
I_5	0.53	4.4×10^{-4}	68	30
I_6	1.14	−95	99	40
II_1	0.41	−113	119	30
II_5	1.74	16	143	30
II_3	2.49	1.78×10^{-3}	159	37
II_8	4.76	−392	154	40
III_1	0.55	1.59×10^{-4}	51	30
IV_1	0.57	-7.85×10^{-4}	175	34
V_1	0.54	3.31×10^{-3}	86	30

Table 3 Intrinsic viscosities and second virial coefficients at different temperatures in toluene for samples I_5 and II_3

Sample	Temp. (°C)	$A_2 \times 10^3$ (cm^3 mol g^{-2})	$[\eta] \times 10^2$ (dl g^{-1})
I_5	17	–	5.0
	20	−0.84	7.0
	22	−0.09	–
	25	–	6.4
	30	0.45	5.7
	32	0.44	–
	35	0.43	6.2
	40	−0.85	5.6
	43	−1.39	–
	45	–	5.8
	50	–	5.1
II_3	20	0.01	–
	21	0.12	10.1
	25	–	9.8
	26	0.16	–
	28	0.30	–
	30	–	9.6
	35	0.25	9.0
	40	–	8.5
	45	–	8.7
	50	–	3.8

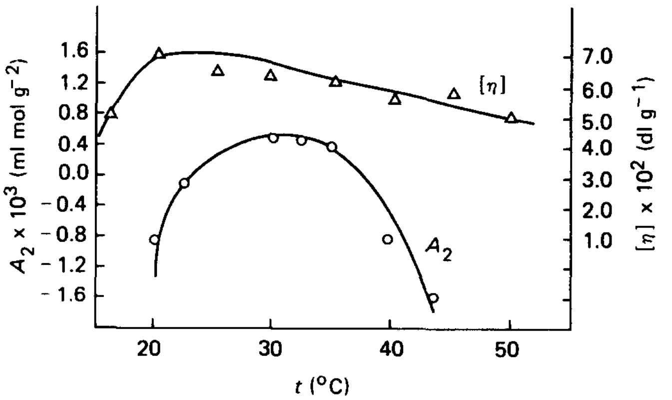


Figure 5 Variation of $[\eta]$ and A_2 with temperature for sample I_5 in toluene

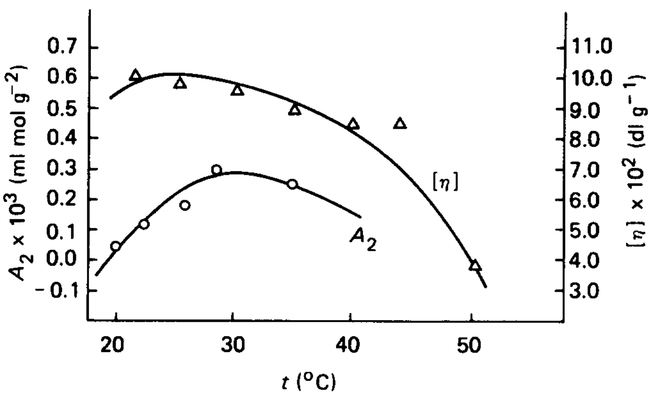


Figure 6 Variation of $[\eta]$ and A_2 with temperature for sample II_3 in toluene

Table 4 The root-mean square radius of gyration and glass transition temperatures for different halogenated poly(dihalophenylene oxides)

Samples	$M_w \times 10^{-4}$	$\langle S^2 \rangle^{1/2}$ (Å)	T_g (°C)
I_5 (TCP)	5.3	68	181
II_1 (4Br-DCP)	4.1	119	215
III_1 (2Br-DCP)	5.5	51	194
IV_1 (2Cl-DBrP)	5.7	175	183
V_1 (TBrP)	5.4	86	196

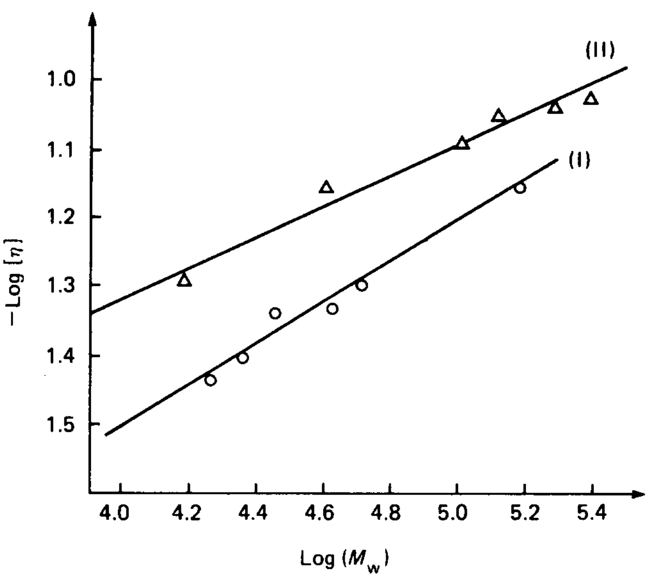


Figure 7 Mark–Houwink–Sakurada plots for the polymers obtained from TCP, sample I (○), and 4Br-DCP, sample II (△), in toluene at 30°C

of the curves for the variation of $[\eta]$ with temperature confirmed the variation of A_2 with temperature in both samples. As the temperature increased $[\eta]$ decreased more sharply for sample I_5 which had a lower molecular weight and more highly branched structure compared to the sample II_3[8,10].

DISCUSSION AND CONCLUSION

The aim of this study was to determine the effects of structure of different halogenated poly(dihalophenylene oxides) on their solution properties. Light scattering is a very useful tool for the characterization of polymers in solution. Hence, when the root-mean-square radii of gyration $\langle S^2 \rangle^{1/2}$ of different halogenated polymers with very similar molecular weights M_w were compared as listed in *Table 4*, the more linear the structure the larger the $\langle S^2 \rangle^{1/2}$ value. All of the samples except I_5 and III_1 have more linear structures according to n.m.r. studies[8,9]. Also, the T_g values indicated the difference. There is a sharp decrease in the values from sample II_1 to samples I_5 and III_1 indicating the softening in the structure due to substantially more branching. Also, the Mark–Houwink–Sakurada plots (*Figure 7*) for poly(dichlorophenylene oxides) synthesized from TCP and 4Br-DCP monomers do not coincide. They give different α and K values indicating different polymer structures. The parameters obtained for samples I and II were $\alpha = 0.327$, $K = 1.5 \times 10^{-3}\,\text{dl g}^{-1}$ and $\alpha = 0.320$, $K = 2.07 \times 10^{-3}\,\text{dl g}^{-1}$, respectively, in reasonable agreement with the previously reported values[8]. In addition, the variation of their refractive index increments with molecular weight showed an asymptotic approach to the same limiting values but the approach is more rapid for sample I compared to sample II, which must have a more linear structure[11]. Hence, it is apparent that bromine in the *para*-position in the monomer favours 1–4 catenation over *ortho*-substitution, leading to a more linear polymer.

The second virial coefficient A_2, which represents the polymer–solvent interaction, is a good indication of the degree of goodness or poorness of the solvent and it usually increases with temperature. For the same polymer (either samples I_5 or II_1) the A_2 values were observed to pass through a maximum as the temperature increased (*Table 3*). This can be explained with two θ-points associated with upper and lower critical solution temperatures[12–18] (*Figures 5* and *6*). Also, the shape of the curve for the variation of intrinsic viscosity with temperature confirmed the variation of A_2 with temperature in both samples. Experimentally, normal and inverted Zimm plots were obtained only at certain temperatures (*Figures 1–4*). However, dramatic distortions of Zimm plots over small temperature ranges were observed as can be followed through the values of A_2 at different temperatures (*Table 2*). This type of behaviour has been observed previously in a system where the *LCST* and *UCST* are close together[18]. Hence, further studies of phase separation will be carried out in our laboratories to confirm the above behaviour in our systems.

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