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Partial specific volume of thermotropic polybibenzoates with different spacers

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Summary

Partial specific volume ($\bar{v}_2^o$) of polybibenzoates with all-methylene and oxyethylene spacers have been determined in chloroalifatic solvents. The polybibenzoate with a heptamethylene spacer exhibits a more expanded state than the ones with one, two and three oxyethylene units in the spacer. A solvent effect on $\bar{v}_2^o$ has been observed. Nevertheless, the values of $\bar{v}_2^o$ in tetrachloroethane are in accord with the calculated by group contributions from rubbery polymers.

Introduction

Liquid crystalline polymers (LCP's) display outstanding properties which have generated a huge increase in their industrial applications as well as in research. Most of the latter is devoted to the synthesis and the structure-related properties of LCP's. However, the shortage of research work on solution properties of LCP's, obviously due to their inherent reduced solubility, is preventing a more profound knowledge of thermodynamic parameters which are essential for basic research in topics as important as conformational-dependent properties (1).

Among LCP's, those incorporating the mesogenic biphenyl group in the main chain are a kind of thermotropic polyesters whose inherent rigidity can be diminished by changing the length and/or structure of the spacer. This approach to the widening of the solubility spectrum of polybibenzoates has been applied in several papers about the solubility parameters of the polymers whose partial specific volumes, $\bar{v}_2^o$, are studied now. In short, the solubility range of polybibenzoates with oxyethylene spacers is significantly widened by increasing the number of oxyethylene units (2) whereas the liquid crystalline character of the polybibenzoates is lost for those with branched spacers (3).

Partial specific volume is a very important polymer magnitude both as input data for the standard techniques of polymer characterization and by itself as information on the state and conformation of the polymer in solution.

The aim of this paper is to analyze the influence of the length and structure of the spacer and the solvent effect on the partial specific volume of several polybibenzoates, namely: poly(heptamethylene p,p'-bibenzoate) (P7MB), poly[oxybis(ethylene oxide) p,p'-bibenzoate] (PDEB), poly[oxytris(ethylene oxide) p,p'-bibenzoate] (PTEB) and poly[oxytetraquis(ethylene oxide) p,p'-bibenzoate] (PTTB). Scheme I shows the general structure of polybibenzoates where A represents the spacer.

The experimental results of $\bar{v}_2^o$ are also compared with the ones obtained by additivity of group contributions.

Experimental

The polybibenzoates studied have been synthesized by melt transesterification of the diethyl ester of p,p'-bibenzoic acid and the corresponding glycol, using isopropyltitanate as catalyst. The values of their

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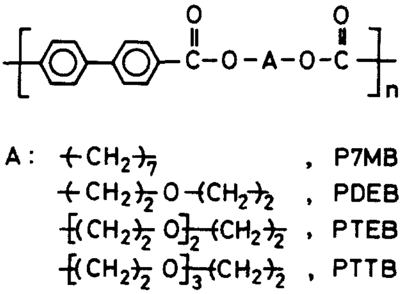

Scheme I

intrinsic viscosities, in chloroform at 25°C, taken from ref.4 for P7MB and from ref.5 for the rest of the polymers, are: 1.03, 1.02, 1.04 and 0.87 dL.g^{-1} for P7MB, PDEB, PTEB and PTTB, respectively.

Chloroform, methylene chloride and tetrachloroethane (Carlo Erba RPE) have been used as solvents for the density measurements and were dried over 4Å molecular sieves before use.

The density of polymer solutions and pure solvents was measured with an Anton Paar DMA 55 digital densimeter. Distilled water and air were used as calibrating substances. The temperature in the measuring cell was regulated with ±0.01° precision. Polymer solutions were prepared by weight. The range of concentration was $1.78 \times 10^{-3} < w_2 < 13.4 \times 10^{-3}$

The partial specific volume at infinite dilution of the studied polymers, $\bar{v}_2^o$, has been obtained by using the rigorous relation

$$\bar{v}_2^o = \rho_1^{-1}[1 - \rho_1^{-1}(\partial\rho/\partial w_2)^o] \qquad (1)$$

where ρ_1 is the density of the pure solvent, and $(\partial\rho/\partial w_2)^o$ is the limiting slope of the solution density vs polymer weight fraction plot.

Results and Discussion

The densities, ρ, of the several polymer solutions of different concentration, w_2, for P7MB, PDEB, PTEB and PTTB have been measured in chloroform and tetrachloroethane at 25.00°C. Also, for P7MB the densities of methylene chloride solutions have be measured at the same temperature.

In Figures 1 and 2 the difference between the density of polymer solutions and pure solvent, $\rho-\rho_1$, is plotted against the weight fraction of the polymer in the solution, w_2, for the four polybibenzoates studied in the selected solvents. The experimental values of $\bar{v}_2^o$ obtained making use of eq.1 are summarized in Table 1, together with the bibliographic specific volumes of the pure polymers, v_2, determined by the flotation method (2,3) and the ones calculated by additivity of group contributions.

From Table 1 we can see that the experimental values of $\bar{v}_2^o$ are sensitive to the spacer structure of the polybibenzoate chains. Thus, the polybibenzoate with an all-methylene spacer (P7MB) exhibits a more expanded state than the ones with one, two and three oxyethylene units in the spacer (PDEB, PTEB and PTTB, respectively).

From the comparison between the specific volume values of each polymer in pure and solution states it is possible to point out an opposite solvent effect, in the studied solvents, between the polybibenzoate with an all-methylene spacer and the ones with oxyethylene spacers. P7MB shows a more expanded state in solution than in solid state, whereas PDEB, PTEB and PTTB either maintain the conformational state or are more contracted. Therefore, the spacer structure

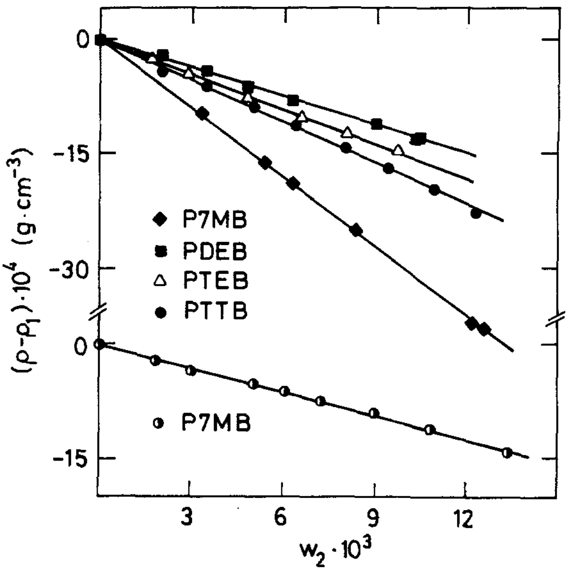

Fig.1. Dependence of the density of polymer solutions on the weight fraction of polymer, w_2, in chloroform (◆,■,△,●) and in methylene chloride (◑), at 25°C.

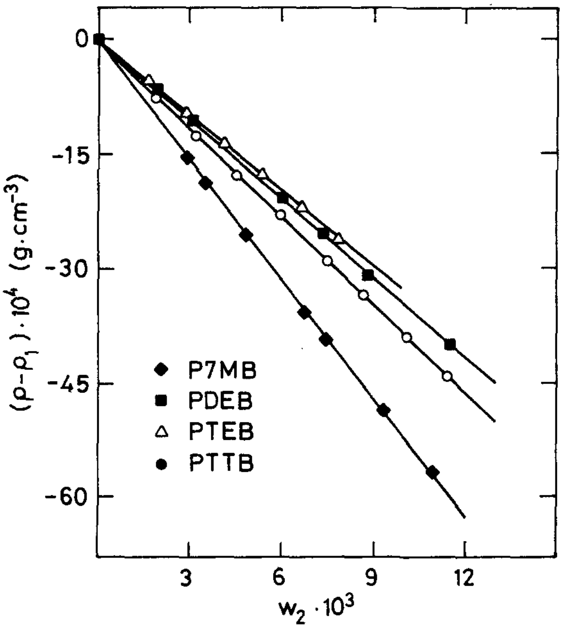

Fig.2. Dependence of the density of polymer solutions on the weight fraction of polymer, w_2, in tetrachloroethane at 25°C.

seems to be responsible for the polymer expansion or contraction under the effect of chlorinated solvents.

Moreover, the spacer length has also influence on the $\bar{v}_2^o$ values. In chloroform, $\bar{v}_2^o$ increases as the number of oxyethylene units in the spacer increases. In each polybibenzoate the polymer chain reaches in chloroform a more contracted state than in tetrachloroethane, and in the case of P7MB in methylene chloride, an intermediate value of $\bar{v}_2^o$ is obtained. This solvent effect could be attributed to the differences in both polarity (6) and solvent quality (3) of the chloroalifatic substances used as solvents.

Unfortunately, it is not possible to compare our results with analogous ones in apolar solvents, because of the insolubility of the polybibenzoates studied.

Finally, the values of the specific volume calculated by group additivity ($v_2^{a\cdot g}$) for the four polybibenzoates have been compared with the corresponding $\bar{v}_2^o$. Since the group contributions for the polymers in their rubbery state should give a better representation of the volume properties in solution, v_2 has been calculated in our case using the Van Krevelen group contributions (7). The values of v_2 thus calculated exceed the experimental ones in tetrachloroethane in less than 6%, although a higher desviation has been obtained in chloroform solution.

Table 1. Partial specific volume of polybibenzoates with different spacer.

Polymer	Solvent	$\bar{v}_2^o$ ($cm^3.g^{-1}$)	v_2 ($cm^3.g^{-1}$)	($v_2^{a\cdot g}$) ($cm^3.g^{-1}$)
P7MB	Cl_2CH	0.814		
	Cl_2CH_2	0.820		
	$Cl_4C_2H_2$	0.835		
	Pure polymer	—	0.806[a]	0.849
PDEB	Cl_3CH	0.733		
	$Cl_4C_2H_2$	0.768		
	Pure polymer	—	0.763[b]	0.789
PTEB	Cl_3CH	0.745		
	$Cl_4C_2H_2$	0.761		
	Pure Polymer	—	0.769[b]	0.807
PTTB	Cl_3C	0.759		
	$Cl_4C_2H_2$	0.783		
	Pure Polymer	—	0.800[b]	0.822

[a]From ref.3. [b] From ref.2.

Conclusions

Partial specific volumes of polybibenzoates are sensitive to both structure and length of the spacer and a solvent effect has been pointed out from the comparison of the partial specific volumes in different solvents and in pure state. The addivity of group contributions gives a fairly good description of tetrachloroethane data.

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