

The Effect of Side Chains on the Partial Specific Volumes of Poly(*o*-Alkylphenyl Methacrylate)s and Polydiitaconates

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Synopsis

Partial specific volumes \bar{v}_2^0 of a series of poly(*o*-alkyl phenyl methacrylate)s and polydiitaconates were determined by density measurements, in toluene and tetrahydrofuran solutions, respectively. The effect of the size and nature of the side groups on partial specific volume is analyzed. Good agreement is found between the experimental \bar{v}_2^0 values and those obtained theoretically from the group contribution method.

INTRODUCTION

Partial specific volume \bar{v}_2 is recognized as an important quantity in connection with the standard techniques of polymer characterization. However, this type of measurement in solution of macromolecules is often restricted by a lack of accurate partial specific volume data. Most values reported in the literature are apparent partial specific volume rather than partial specific volume, since the extrapolation from density measurements is usually omitted. In spite of the often small differences between these parameters, a direct determination of the partial specific volume \bar{v}_2 of dissolved macromolecules is needed.

The partial specific volume of a polymer in solution depends on both segment–segment and segment–solvent interactions. Therefore, it can be a useful parameter in order to obtain information on the state and conformation of a polymer in solution. Experimentally it has been found that \bar{v}_2 depends on solvent,^{1–3} concentration,^{2–4} and temperature.⁴

The value of \bar{v}_2^0 (determined at infinite dilution) usually depends on molecular weight for low molecular weight and attains limiting constant values at sufficiently high molecular weight. Schulz and Hoffman⁵ found that \bar{v}_2 is practically independent of molecular weight at above 10^4 g/mol for polystyrene and poly(methyl methacrylate) in a number of solvents. Although the dependence of many properties of polymethacrylates and polyitaconates with

the bulkiness of the side group have been described in the literature,⁶⁻¹⁰ there is not yet clear as far as the correlation between the chemical structure of the polymer and its density is concerned.

In order to investigate the influence of the length of the ester substituents on partial specific volume in one solvent and verify the generally expected additive character of \bar{v}_2^0 for two series of polymers, we report a systematic study on the partial specific volume for a series of poly (*o*-alkylphenyl methacrylate)s [poly(phenyl methacrylate) (PPh), poly(2,6-dimethylphenyl methacrylate) (PDMPH) and poly(2,6-diisopropylphenyl methacrylate) (PDPPH)]; poly(di-*n*-alkyl itaconate)s [polydimethyl (PDMI), polydiethyl (PDEtI), poly(di-*n*-propyl) (PDPI), and poly(di-*n*-butyl) (PDBI) itaconates]; and poly-dibenzylitaconate (PDBzI).

EXPERIMENTAL

Monomers and Polymers

Methacrylate and polymethacrylate preparations were performed according to the techniques described previously.¹¹ All the polymerizations were done in the same conditions in order to ensure similar tacticities. The diesters of itaconic acid were prepared and purified as reported in previous works.^{12,13} Monomers were polymerized in bulk or in solution with 2,2'-azobisisobutyronitrile (AIBN) as initiator.^{12,13}

The weight-average molecular weights (\bar{M}_w) of the fractions was determined by size exclusion chromatography (SEC). Number-average molecular weight (\bar{M}_n) of the fractions was determined by membrane osmometry. We have chosen polymer fractions having molecular weights above 10^5 , corresponding to the range of \bar{M}_w , where the \bar{v}_2 should have attained their constant limiting values, and with polydispersities $\bar{M}_w/\bar{M}_n = 1.2-1.4$.

Densimetry

Solvents used in densimetry measurements were Merck p.a. All of them were first dried before using.

The partial specific volume was determined at 298 K by pycnometry for several polymer solutions, as well as pure solvent. An Anton Paar DMA 55 digital densitometer was also used. Both methods give the same values. Measurements were made in toluene for polymethacrylates and in tetrahydrofuran (THF) for polydiitaconates. Polymer solutions were prepared by weight. The range of concentration (expressed as polymer weight fraction w_2) was $4.0 \times 10^{-3} \leq w_2 \leq 15.0 \times 10^{-3}$ for polymethacrylates and $2.0 \times 10^{-3} \leq w_2 \leq 7.5 \times 10^{-3}$ for polydiitaconates.

RESULTS AND DISCUSSION

Partial specific volume \bar{v}_2^0 of the polymers has been calculated from density measurements through the equation:

$$\bar{v}_2^0 = \rho_1^{-1} \left[1 - \rho_1^{-1} (\partial \rho / \partial w_2)^0 \right] \quad (1)$$

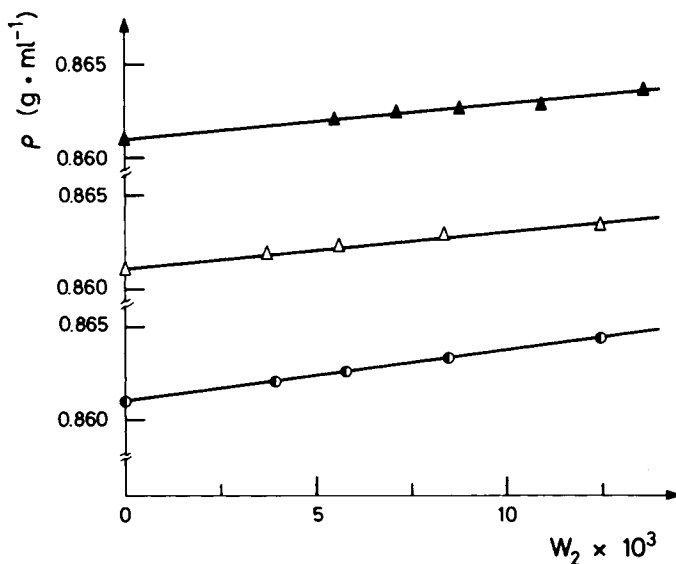


Fig. 1. Variation of the solution density ρ with polymer weight fraction w_2 at 25°C for: (●) PPh; (△) PDMPH; (▲) PDPPH.

where ρ_1 is the solvent density and $(\partial\rho/\partial w_2)^0$ is the slope of the plot of the solution density ρ vs. polymer weight fraction w_2 ; superscript zero means extrapolated magnitude at infinite dilution. Figures 1 and 2 show the dependence of ρ on w_2 for the polymers in the solvents used. The values of \bar{v}_2^0 obtained at 298 K are summarized in Tables I and II.

We can see that the experimental values of partial specific volume in solution \bar{v}_2^0 show variation when the substituent of the repeat unit changes. The \bar{v}_2^0 values increase with the increasing of the degree of substitution in the aromatic ring, and, therefore, with the bulkiness of the side chain in the case of poly(*o*-alkylphenyl methacrylate)s (see Table I).

We have found similar variation in the series of polydiitaconates: i.e., the \bar{v}_2^0 value also increases with the increasing of the size of the lateral chain (see Table II). The sequence of the variation of \bar{v}_2^0 values is PPh < PDMPH < PDPPH in the first series and the \bar{v}_2^0 values increase with the increasing of the aliphatic chain in polydiitaconates. The variation of \bar{v}_2^0 in this series is PDMI < PDEI < PDPI < PDBI.

It is interesting to compare \bar{v}_2^0 in solution with values measured on pure polymers. In the literature, density values have been given by Veličković and Vasović¹³ only from specific refractivities measurements, for some polydiitaconates: PDMI, PDEI, and PDBI. These values are higher than our experimental results obtained from density measurements, which could be due to the fact that specific refractivities are not an accurate enough method as density measurements.

Since the density in bulk is not known for these polymethacrylates and polydiitaconates, we cannot compare directly with our values of \bar{v}_2^0 in solution. However, we can attempt an indirect comparison through calculated values, making use of the concept of additivity of group contributions to the molar volume. Taking the group contributions given by Van Krevelen¹⁴ for

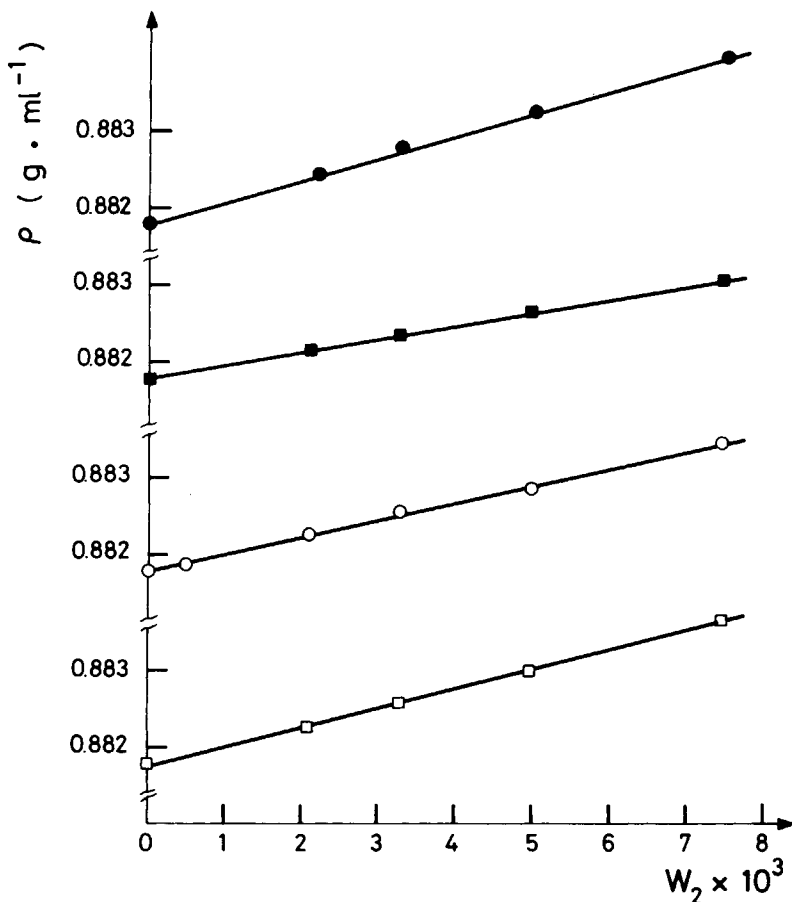




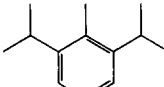

Fig. 2. Variation of the solution density ρ with polymer weight fraction w_2 at 25°C for: (●) PDMI; (■) PDBI; (○) PDPI; (□) PDEI.

glassy polymers at 298 K (T_g of these polymers is above 298 K), we can calculate the molar volumes.

Now we compare the experimental and calculated specific volumes, for polymethacrylates and polydiitaconates. The results are also summarized in Tables I and II. As we can see, the experimental values of partial specific volume in solution show a systematic deviation from the values calculated in bulk. Taking into account the mean value of this systematic deviation, we can say that the experimental values here determined for our polymers are adequately predicted by the calculated ones.

However, values of v_{sp} calculated from additivity of group contributions given by Van Krevelen for glassy polymers V_g and those obtained for rubber polymers V_r are 0.834 and 0.799 for poly(phenyl methacrylate) and 0.821 and 0.791 for poly(dibenzyl itaconate), respectively.¹⁵ The values of \bar{v}_2^0 measured in solution are very close to v_{sp} calculated for rubber polymers (V_r) while v_{sp} calculated from V_g are noticeably higher (differences about $0.04 \text{ cm}^3 \text{ g}^{-1}$) in the case of these two polymers with aromatic rings.

TABLE I
 Partial Specific Volume \bar{v}_2^0 of Poly(phenyl Methacrylates) and
 Poly(*o*-Alkylphenyl Methacrylates)
 in Toluene at 25°C

Polymer	Side group	\bar{v}_2^0 (cm ³ g ⁻¹)	v_{sp}^a (cm ³ g ⁻¹)	Difference calculated solution	
				$(V_g)^b$	\bar{v}_2^0
Poly(phenyl methacrylate) (PPh)		0.789	0.834 0.799 ^c	0.045 0.010 ^c	
Poly(2,6-dimethylphenyl methacrylate) (PDMPH)		0.880	0.894	0.013	
Poly(2,6-diisopropylphenyl methacrylate) (PDPPH)		0.922	0.956	0.039	
Poly(methyl methacrylate) (PMM _e) ^d		0.810 ^b	0.864	0.054	





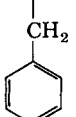
^a v_{sp} values calculated from Van Krevelen group contributions (V_g).¹⁴

^bFrom Ref. 14.

^c v_{sp} values calculated from Van Krevelen group contributions (V_g).¹⁴ Calculated (V_g) - solution (\bar{v}_2^0).

^dThis polymer is given for comparison.

TABLE II
 Partial Specific Volume \bar{v}_2^0 and Specific Volume v_{sp} of Polydiitaconates
 in Tetrahydrofuran at 25°C

Polymer	Side group	\bar{v}_2^0 (cm ³ g ⁻¹)	v_{sp}^a (cm ³ g ⁻¹)	Difference calculated solution	
				$(V_g)^b$	\bar{v}_2^0
Poly(dimethyl itaconate) (PDMI)		0.794	0.793	0.007	
Poly(diethyl itaconate) (PDEIt)		0.815	0.843	0.028	
Poly(dipropyl itaconate) (PDPIt)		0.844	0.881	0.038	
Poly(dibutyl itaconate) (PDBIt)		0.912	0.910	-0.001	
Poly(dibenzyl itaconate) (PDBzIt)		0.794 ^c	0.821 0.791 ^d	0.027 0.003 ^d	

^a v_{sp} values calculated from Van Krevelen group contributions (V_g).¹⁴

^b v_{sp} values from Ref. 14.

^cIn 1,4-dioxane at 25°C.¹⁵

^dCalculated (V_g) - Solution (\bar{v}_2^0).

In this respect the size of the substituents seems to be of predominant importance and can compensate for the other group contributions.

A smaller value of \bar{v}_2^0 for PPh in comparison with that obtained for PMMA is observed in toluene at 298 K and is also observed for PDBzI in comparison with that obtained for PDEI (Table II). In both cases the polymers are more contracted when the pendant groups attached to the main chain of the polymer have a phenyl group instead of a methyl group. This behavior is similar to that observed in poly(methylphenyl siloxane) recently reported.³

The partial specific volume \bar{v}_2^0 of the two series of polymers studied increases with increasing the volume of the side chain. The group contributions from Van Krevelen have been used, and we can show that the calculated values are in an acceptable agreement with the experimental values. The calculated \bar{v}_2^0 value for PPh is in good agreement when it is calculated from Van Krevelen group contributions for rubber polymers.¹⁴

In the case of poly(diethyl itaconate) and poly(dibenzyl itaconate), relative to poly(dimethyl itaconate), the incorporation of phenyl rings also gives a denser polymer.

Finally we can conclude that partial specific volume \bar{v}_2^0 is considerably affected by the size and nature of the side group of the polymer and that the experimental values can be well reproduced by using the group contribution method of Van Krevelen.

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