

Density and Thermal Expansion of a Trifluoropropylsiloxane Polymer in Solution

INTRODUCTION

The partial specific volume of polymers in solution is a quantity required for many of the standard techniques of polymer characterization. Extensive compilation of data of \bar{v}_2^0 for many polymers can be found in Brandrup and Immergut.¹

In general, \bar{v}_2^0 in solution is close to the specific volume of the bulk polymer; however, the solvent has a certain influence. Differences in \bar{v}_2^0 can be found depending on the solvent, but these differences are usually small for nonionic polymers. The molecular weight of the polymer can also influence the value of \bar{v}_2^0 , but only in the range of low molecular weights, \bar{v}_2^0 being constant for M above 10^4 .²

Of the siloxane family of polymers, the one most widely studied is poly(dimethylsiloxane) (PDMS). The partial specific volume has also been reported for poly(methylphenylsiloxane) (PMPS).³

Here, we report \bar{v}_2^0 and its temperature variation for another unsymmetrical siloxane polymer: poly(methyltrifluoropropylsiloxane) (PMTFPS). Recently, we have reported on networks of PMTFPS and have studied its swelling with different solvents, as a function of temperature.⁴ Data of \bar{v}_2^0 are companion to that study.

EXPERIMENTAL

Polymer

A sample of PMTFPS was generously supplied by Dow Corning Co. to Dr. M. A. Llorente (UNED).⁵ This polymer contains about 0.5% vinyl groups (same polymer used to prepare networks for stress-strain⁵ and swelling⁴ measurements). The molecular weight of the sample has been determined by viscometry. Intrinsic viscosity in ethylacetate at 25°C is $[\eta] = 0.852$ dL/g which corresponds to⁶ $\bar{M}_w = 8.71 \times 10^5$.

Solvents

These were from Carlo Erba of RPE quality. They were used without previous treatment.

Density

Density of solvent and of polymer solutions were measured with a vibrating-tube digital densimeter (Anton Paar DMA 55, Austria). Distilled water and air were used as calibrating substances. Polymer solutions were prepared by weight. The range of concentrations covered was $\omega = 0 - 15.535 \times 10^{-3}$ (ω being polymer weight fraction). The temperature of measurement was regulated to $\pm 0.01^\circ\text{C}$.

RESULTS AND DISCUSSION

We calculated the partial specific volume of the polymer from measurements of solution density ρ as a function of solute concentration ω using³

$$\bar{v}_2^0 = \rho_1^{-1} \left(1 - \rho_1^{-1} \left(\frac{\partial \rho}{\partial \omega} \right)^0 \right)$$

TABLE I
 Partial Specific Volume of Poly(methyltrifluoropropylsiloxane)
 and Comparison with Other Siloxane Polymers

Polymer	Solvent	Temperature (°C)	\bar{v}_2^0 (cm ³ · g ⁻¹)	$\alpha \times 10^3$ (K ⁻¹)
PMTFPS	BuCl	25	0.779 ^a	
	MEK	25	0.776 ^a	
	EtOAc	15	0.773 ^a	
	EtOAc	25	0.780 ^a	0.9 ^d
	EtOAc	45	0.801 ^a	1.3 ^d
PMPS	BuCl	25	0.861 ^b	
	Cyclohexane	25	0.889 ^b	
PDMS	MEK	10	1.0180 ^c	1.00 ^d
	MEK	20	1.0282 ^c	
	MEK	35	1.0468 ^c	1.20 ^d

^a This work.

^b Ref. 3.

^c Ref. 7.

^d Calculated from \bar{v}_2^0 as explained in text.

where subscript 1 refers to pure solvent and superscript zero to $\omega \rightarrow 0$ limiting value. In the range of very dilute solutions used here, the density is practically linear with ω . We therefore obtain $(\partial\rho/\partial\omega)^0$ from the slope of the linear ρ vs. ω regression. The results thus determined for \bar{v}_2^0 of PMTFPS are shown on Table I.

Methylethyl ketone (MEK) and ethylacetate (EtOAc) are good solvents of PMTFPS while *n*-butyl chloride (BuCl) is a poor solvent for the polymer.⁴ We can see that no specific solvent effects are shown by the \bar{v}_2^0 values. \bar{v}_2^0 is practically the same in all three solvents at 25°C.

We can compare PMTFPS to the other siloxane polymers PDMS and PMPS. Replacing a methyl by a phenyl group produces an increase in the polymer density. Replacing the methyl by a trifluoropropyl group should produce an even greater increase in density. The values of \bar{v}_2^0 for these three polymers at 25°C are given in Table I. PMTFPS has the lower \bar{v}_2^0 .

We can use the additivity of groups method⁸ to estimate the differences due to group replacement and compare them with the observed ones. The molar volumes corresponding to methyl, phenyl, and trifluoropropyl groups are, respectively: 22.8, 64.65, and 67.65 cm³/mol.⁸ Starting with the value of \bar{v}_2^0 for PDMS $\bar{v}_2^0 = 1.034$ cm³/g we calculated the partial specific volumes that could correspond by replacing one methyl group by a phenyl group or by a trifluoropropyl group, with the results: $\bar{v}_2^0 = 0.870$ cm³/g for PMPS, and $\bar{v}_2^0 = 0.778$ for PMTFPS. We can see that agreement between these estimates and the corresponding experimental values is excellent.

We have measured \bar{v}_2^0 of PMTFPS at three temperatures in EtOAc. The results are shown on Table I. The temperature variation of \bar{v}_2^0 for PMTFPS is very similar to that of PDMS. In Table I we compare both temperature variations in the form of thermal expansion coefficients, $\alpha = d \ln \bar{v}_2^0 / dT$, (calculated as quotient of differences, $\alpha = (\Delta\bar{v}_2^0 / \bar{v}_2^0) / \Delta T$ between two temperature values). We can see that the mean value of α in PMTFPS is very similar to α of PDMS.

The conclusion is then that the trifluoropropyl substituent increases markedly the density of the polymer with respect to PDMS, but that the thermal expansion is of similar magnitude in both polymers.

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