

Apparent Specific Volumes of Styrene-Methyl Methacrylate Copolymers of Varying Microstructure and Composition

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Apparent specific volumes of styrene-methyl methacrylate copolymers of varying architecture and composition were determined in *p*-xylene at $30.00 \pm 0.01^\circ\text{C}$. The results were compared with the theory of Inagaki which assumes the additivity of molar volumes of diads rather than of monomeric units. The experimental data are in agreement with the theory. The specific volumes of statistical copolymers can be described by those of the parent homopolymers and the alternating copolymer with the diad frequencies deduced from the copolymerization kinetics, while those of two or three block copolymers are nearly the composition average of those of the parent homopolymers, since the contribution from the diads of unlike monomer units is negligible in such block polymer chains.

INTRODUCTION

About a decade ago one of us developed a theory which relates the apparent specific volume of a copolymer with its composition and microstructure, *i.e.*, the sequence length distribution.^{1,2)} In spite of the efforts to substantiate the theory, the earlier experimental test turned out to be unsatisfactory, mainly because of the lack of adequate reference samples of a copolymer which should have a given composition but entirely different sequence-length distribution.³⁾ However, the subsequent development in the art of copolymerization⁴⁻⁶⁾ had enabled us to have good reference and test samples from a given comonomer pair.⁷⁻¹¹⁾ Therefore, we renewed the interest for testing the earlier theory. We will report the results herein.

EXPERIMENTAL PART

Polymer samples tested were styrene-methyl methacrylate (ST-MMA) copolymers of three different microstructures: They are statistical copolymers⁷⁾ prepared by radical copolymerization method, block copolymers of PMMA-PST-PMMA type⁸⁾ and of PST-PMMA type⁹⁾ prepared by anionic polymerization method; and alternating copolymers^{10,11)} prepared by the complexed copolymerization method of

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Hirooka⁶⁾ using alkyl-aluminumhalide catalysts. The solvent was *p*-xylene, which was refluxed over sodium wire and distilled twice just before use.

Density measurements were made either by 25 ml Welde type pycnometers or by a buoyancy method¹²⁾ with a Cahn RG automatic electrobalance (Cahn Instr. Co., Paramount, Calif., U. S. A.).¹³⁾ In the latter, two nearly identical sinkers with the volume of about 0.25 ccm were suspended by thin wire from each end of the balance-arm, one being immersed in a constant-density liquid (usually the solvent) and the other (*i.e.*, the sample sinker) being immersed in a solution. The balance can be set to full scale recorder ranges (100 divisions) from 0.02 mg to 1 g and is sensitive to 0.1 μ g. However, for a routine operation in the buoyancy measurements, it is more convenient to operate it at ± 1 μ g accuracy level. We can determine the density value in 6 decimal places. All the measurements were carried out at $30.00 \pm 0.01^\circ\text{C}$ with a doubly thermostated bath system.³⁾ Usually the measurements were made at four different concentrations in 0.5~2.2 wt% range. The concentration dependence of apparent specific volumes was found to be negligibly small. All the results are summarized in Table I.

Table I. Summary of the Apparent Specific Volume Data of Styrene-methyl Methacrylate Copolymers of Varying Microstructure in *p*-xylene 30.0°C

Code	ST-content mol% (wt%)	(\bar{M}_c/N)	R	v_2^* observed	v_2^* calculated (by Eq. 8) (by Eq. 7)	
PST	0	104.1	0	0.9233	—	—
PMMA	0	100.1	0	0.8152	—	—
Alternating copolymer	50.0 (51.0)	102.1	100	0.8594	0.8699	—
<i>Statistical Copolymers</i>						
I-SM 25	23.8 (24.4)	101.1	44	0.836	0.8413	0.8371
SM3-1	29.9 (30.8)	101.2	52	0.841	0.8481	0.8432
II-SM 50	48.3 (49.3)	102.0	67	0.863	0.8680	0.8613
II-SM 75	74.4 (75.1)	103.8	46	0.889	0.8957	0.8950
<i>Block Copolymers</i>						
MSM 60B	28.2 (29.0)	101.2	0	0.846	0.8463	
MSM 27B	40.5 (41.4)	101.7	0	0.858	0.8595	
MSM 11B	85.1 (85.6)	103.5	0	0.908	0.9069	
SM 46B	44.0 (45.0)	101.9	0	0.864	0.8633	
SM 63B70	67.6 (68.5)	102.9	0	0.888	0.8886	

RESULTS AND DISCUSSION

According to Inagaki's theory,¹⁾ the apparent specific volume v_2^* of an *AB*-binary copolymer with the average *A*-content *m* (by mole fraction) can be given as

$$v_2^* = (-N/\bar{M}_c)(P_{aa}\mathbf{B}_A + 2P_{ab}\mathbf{B}_{AB} + P_{bb}\mathbf{B}_B) \quad (1)$$

$$\bar{M}_c = N[mM_A^\circ + (1-m)M_B^\circ] \quad (2)$$

where \bar{M}_c is the number average molecular weight of the copolymer; *N* is the (number)-average degree of polymerization; P_{aa} , P_{ab} , and P_{bb} are the corresponding diad

frequencies; and M_A° and M_B° are the molar weights of the monomer units. The parameters $\mathbf{B}_A, \mathbf{B}_B$, and \mathbf{B}_{AB} are the binary cluster integrals for the corresponding diads and solvent molecules. They can be determined from the apparent specific volumes of the parent homopolymers v_A^* and v_B^* and the alternating copolymer v_{AB}^* as

$$v_A^* = -\mathbf{B}_A/M_A^\circ, \quad v_B^* = -\mathbf{B}_B/M_B^\circ \quad (3a, b)$$

$$v_{AB}^* = -2\mathbf{B}_{AB}/(M_A^\circ + M_B^\circ) \quad (3c)$$

The apparent specific volume v_2^* of the solute copolymer can be defined from the solution and solvent (component 1) densities ρ and ρ_1 as

$$1/\rho = g_1 v_1 + g_2 v_2^* \quad (4)$$

where $v_1 = 1/\rho_1$ is the specific volume of the pure solvent, and g_1 and g_2 are the weight fractions of the solvent and solute, respectively, in the solution.

To correlate the apparent specific volume of a copolymer with those of the parent homopolymers and the alternating copolymer, we need to know the diad frequencies of the given copolymer. The diad frequencies can be conveniently described in terms of Harwood-Ritchey's run number R ,¹³⁾ which is defined as "the average number of sequences (runs) occurring in a copolymer per 100 monomer units." Therefore, the diad frequencies are

$$P_{aa} = m - R/200, \quad P_{bb} = (1 - m) - R/200 \quad (5a, b)$$

$$P_{ab} = P_{ba} = R/200 \quad (5c)$$

Obviously we have $R=0$ and $R=100$, respectively, for a block copolymer and for a strictly alternating copolymer. On the other hand, for a statistical copolymer obtained by a radical copolymerization in which only two reactivity ratios r_a and r_b are involved, we obtain a convenient expression¹¹⁾ of R from the Lewis-Mayo feed-product compositional relationship⁵⁾ and the Harwood-Ritchey run number equation¹⁴⁾ as

$$R = \frac{400m(1-m)}{1 + \{1 + 4m(1-m)(r_a r_b - 1)\}^{1/2}} \quad (6)$$

It should be noted that Eq. 6 is valid only for a low-conversion or an instantaneous copolymer. Employing $r_a = 0.52$ and $r_b = 0.46$ for radically prepared ST-MMA statistical copolymers,⁵⁾ we calculated the values of R which are listed in Table I.

Now combining Eqs. 1~5, we have

$$v_2^* = x v_A^* + (1-x) v_B^* + (N/\bar{M}_c)(R/100) \Delta \quad (7a)$$

$$\begin{aligned} \Delta &= \frac{1}{2} [(M_A^\circ + M_B^\circ) v_{AB}^* - M_A^\circ v_A^* - M_B^\circ v_B^*] \\ &= \frac{1}{2} (\mathbf{B}_A + \mathbf{B}_B) - \mathbf{B}_{AB} \end{aligned} \quad (7b)$$

where $x = m \bar{M}_A^\circ (N/M_c)$ is the weight fraction of A in the copolymer. If the additivity of the apparent molar volumes is assumed, (*i. e.*, $\Delta = 0$) then the v_2^* of a copolymer will be the weight average of those of the parent homopolymers:

$$v_2^* = x v_A^* + (1-x) v_B^* \quad (8)$$

Using the values of v_2^* for PST, PMMA, and ST-MMA alternating copolymer, we have calculated v_2^* for the statistical and block copolymers by Eqs. 7 and 8. For the

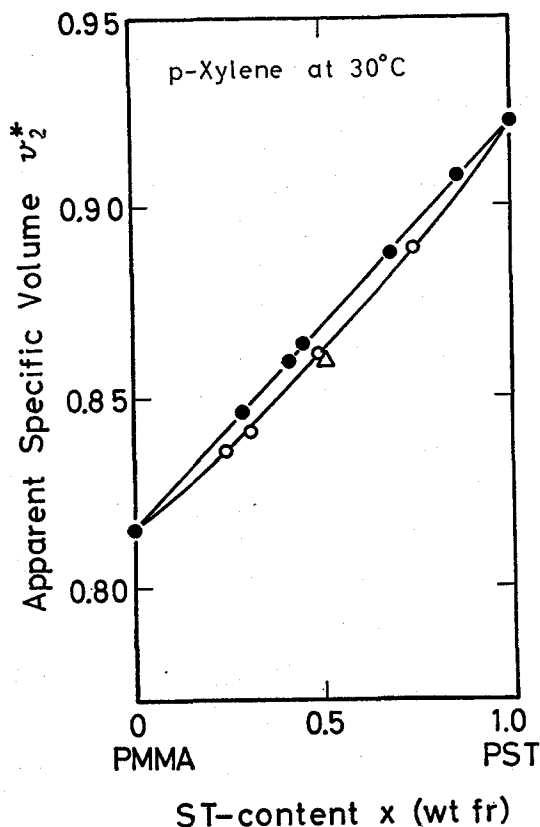


Fig. 1. Apparent specific volumes v_2^* versus ST-content x (by weight fraction) for ST-MMA copolymers of different microstructure determined in *p*-xylene at 30.0°C: Solid circles for block copolymers; open circles for statistical copolymers; and triangle for alternating copolymer (see Table I). Two curves indicate v_2^* versus x relations calculated by Eqs. 7 and 8.

block copolymers Eqs. 7 and 8 give identical results. The calculated values are listed in Table I. The experimental and calculated values of v_2^* are compared also in Fig. 1, in which v_2^* are plotted against x . Apparently the additivity in v_2^* is a good approximation for the block copolymers. While for the statistical copolymers the value of A is only 1.16₂, which results in a very small but still distinguishable difference between the values of v_2^* calculated by Eqs. 7 and 8. The former Eq. 7 seems to be a better approximation for the ST-MMA statistical copolymers.

Previously density data of Nakajima *et al.*¹⁵) on vinylacetate (VA) and vinylchloride (VC) statistical copolymers were examined.¹⁾ The data are reevaluated and summarized in Table II. For the VA-VC copolymers the additivity in v_2^* , Eq. 8, is a poor approximation. While the values of AB calculated by Eq. 7 are in reasonable agreement among those of varying VA-content. These results suggest that the diad model¹⁾ provides a better approximation for the microstructure-dependence of the apparent specific volume of a copolymer.

Apparent Specific Volumes of ST-MMA Copolymers

Table II. Summary of the Apparent Specific Volume Data of Vinylacetate-Vinyl Chloride Statistical Copolymers in Cyclohexanone¹⁵⁾

VA-content mole% (wt%)	Run number ^{a)} <i>R</i>	(\bar{M}_c/N)	v_2^* (obs) (ccm·g ⁻¹)	v_2^* (calcd by Eq. 8) (ccm·g ⁻¹)	B_{AB} (by Eq. 7) (ccm)
100 (100)	0	86.0	0.89	—	—
78 (83.0)	35.1	80.8	0.80	0.856	46.94
59 (66.4)	49.9	76.4	0.77	0.823	51.72
38 (45.8)	48.6	71.4	0.73	0.782	52.19
0 (0)	0	62.5	0.69	—	—

a) Calculated by Eq. 6 with the reactivity ratios $r_a=0.65$ and $r_b=1.35$ (T. Kimura *et al.*)¹⁶⁾

REFERENCES

- (1) H. Inagaki, *Makromol. Chem.*, **75**, 217 (1964).
- (2) Y. Kobatake and H. Inagaki, *ibid.*, **40**, 118 (1960).
- (3) Y. Murakami, MS dissertation submitted to Department of Polymer Chemistry, Kyoto University, 1964.
- (4) See for example, M. Szwarc, Carbanions, Living Polymers, and Electron-Transfer Processes, Interscience Publishers, New York, 1968.
- (5) G. E. Ham, ed., Copolymerization, Interscience Publishers, New York, 1964.
- (6) M. Hirooka, *Kobunshi*, **16**, 1172 (1967); M. Hirooka, H. Yabuuchi, J. Iseki, and Y. Nakai, *J. Polym. Sci.*, A1-6, 1381 (1968).
- (7) T. Kotaka, Y. Murakami, and H. Inagaki, *J. Phys. Chem.*, **72**, 829 (1968).
- (8) H. Ohnuma, T. Kotaka, and H. Inagaki, *Polymer*, **10**, 501 (1969).
- (9) T. Kotaka, T. Tanaka, and H. Inagaki, *Polymer J.*, **3**, 327 (1972).
- (10) Y. Murakami, Ph. D. Dissertation, Kyoto University, 1968.
- (11) T. Kotaka, T. Tanaka, H. Ohnuma, Y. Murakami, and H. Inagaki, *Polym. J.*, **1**, 245 (1970).
- (12) See for example, F. Daniels, T. H. Mathews, P. Bender, G. W. Murphy, R. A. Alberty, *Experimental Physical Chemistry*, McGraw-Hill, New York, 1949 (4th ed.) pp 427-432.
- (13) See for example, L. Cahn and H. Schutz, *Anal. Chem.*, **35**, 1729 (1963).
- (14) H. J. Harwood and W. M. Ritchey, *J. Polym. Sci.*, **B2**, 601 (1964).
- (15) A. Nakajima, H. Sotobayashi, and I. Sakurada, *Kobunshi-Kagaku*, **14**, 566 (1957).
- (16) T. Kimura and K. Yoshida, *Kagaku to Kogyo*, **32**, 223, 341 (1958).