Effects of chain ends and molecular weight on specific volumes of anionic polystyrene melts

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(Received 9 August 1976; revised 14 September 1976)

Specific volumes of anionic polystyrenes prepared by butyl lithium initiation have been measured at temperatures between 110° and 237°C. Molecular weights of the fractions studied ranged from 2500 to 700 000. Plots of isothermal specific volume against reciprocal molecular weight (M^{-1}) are fitted by two straight lines intersecting at a molecular weight near 10 000. This parallels the behaviour of thermally initiated polystyrene fractions, which have different end-groups. Volumes attributable to end-groups are greater for the anionic polymers. The specific volume–molecular weight–temperature relations in the $M \leqslant 10\,000$ region are explained quite well by the equation of Francois and coworkers, in terms of end-group volumes and a uniform volume contribution from internal repeating units. Restraints on the motion of the butyl end-groups in these polymers by the attached polystyrene chain appear to be temperature dependent in terms of this model. Specific volumes of polymers with $M \geqslant 10\,000$ are affected by chain ends and by variation of the volumes of non-end repeating units with molecular weight. The present results parallel those which have been reported for partial specific volumes of polystyrenes in dilute solution and suggest that the same factors operate in both cases.

INTRODUCTION

A previous article[1] from this laboratory has reported specific volume–temperature–molecular weight relations for anionic polystyrenes with molecular weights between 9400 and 700 000, at 170°–237°C. Volumes attributable to end-groups were shown to differ between anionic and thermally initiated polystyrenes. More data have now been obtained which allow extension of these results to molecular weights and temperatures as low as 2500 and 110°C, respectively.

The earlier results were analysed according to the well-known theoretical expectation that specific volume at a given temperature will be rectilinear in reciprocal molecular weight[2–4]. This relation implies that variation of specific volume with molecular weight is due only to the effects of chain ends. Francois and coworkers[5,6] have recently disputed this theory and have presented evidence showing that this relation is valid only for low molecular weight polymers. Specific volumes of high molecular weight samples seem to be influenced also by variation of segment density with increasing molecular weight. End-group effects were stated to be predominant in bulk thermally initiated polystyrene liquids only at molecular weights less than 10 000[6]. The additional anionic polystyrene data reported here permit discrimination between the two models and provide a direct test of the theoretical predictions of Francois *et al.*[6]. This is the first such experimental application of the latter theory to melts of commercially available anionic polystyrenes which are widely used in polymer science.

EXPERIMENTAL

The anionic polystyrene samples studied were narrow molecular weight distribution polymers supplied by the Pressure Chemical Company (Pittsburgh).

The specific volumes reported earlier[1] were measured by melt extrusion[7] and static melt volume[8] techniques which are described in the cited references. These methods have been shown to provide specific volume values which coincide with those expected from dilatometry and other techniques[7–9]. The standard deviation of replicate measurements is about 0.001 cm^3/g[7].

The additional data reported here were obtained by mercury dilatometry. The dilatometers used were essentially as described by others[10,11]. The glass capillaries attached to the dilatometers were calibrated by weighing mercury[10] and the relative density values measured were converted to absolute densities by calibrating with a polystyrene sample whose density was determined by a pycnometric method[10,12]. The density of the anionic polystyrene with 2490 molecular weight was found to be 0.9970 g/cm^3 at 121°C, in this connection. The densities measured by the three techniques used in this work are shown below to be consistent.

Polymer molecular weights

Molecular weights of these polymers were given by the supplier and were verified by our own measurements of limiting viscosity numbers or by gel permeation chromatography. Molecular weight measurements were made as far as possible with specimens which had already been used in specific volume experiments, to allow for possible degradative effects. Particular attention was paid to the lowest molecular weight polymers and solution viscosities in these instances (samples 11b and 12b) were measured with an automatic timer in an apparatus with flow times reproducible to 0.01 sec. Up to 10 measurements were made at

Table 1 Molecular weights of anionic polystyrenes

		Intrinsic viscosity			$[\eta] = K\bar{M}_v^{\alpha}$					
Sample code[a]	As-received molecular weight[a]	Solvent	Temperature (°C)	$[\eta]$ (dl/g)	$K \times 10^4$ (dl/g)	α	Ref	Sample thermal history (°C)	$\bar{M}_v$	$\bar{M}_w$ (G.p.c.)
6a	8.60×10^5	Toluene	25.0	1.820	1.7	0.69	13	217	7.08×10^5	–
3a	4.11×10^5	Toluene	25.0	1.220	1.34	0.71	14	237	3.76×10^5	–
4a	9.72×10^5	Toluene	25.0	0.434	1.34	0.71	14	237	8.92×10^5	–
7a	5.10×10^4	Toluene	25.0	0.229	1.7	0.69	13	217	5.25×10^4	–
7b	3.70×10^4	–	–	–	–	–	–	260	–	3.54×10^4
2a	1.98×10^4	Toluene	25.0	0.132	1.7	0.69	13	237	1.55×10^4	–
2b	2.04×10^4	Toluene	25.0	0.148	1.7	0.69	13	237	1.86×10^4	–
8a	1.03×10^4	Toluene	25.0	0.097	10	0.50	15	204	9.40×10^3	–
8b	1.0×10^4	–	–	–	–	–	–	230	1.06×10^4	
11b	4.0×10^3	Benzene	30.0	0.0760	10	0.50	15	Nil	5.78×10^3	
12b	2.1×10^3	Benzene	30.0	0.0499	10	0.50	15	Nil	2.49×10^3	

[a] Pressure Chemical Company, Pittsburgh

each concentration to ensure accurate readings.

Table 1 lists supplier's molecular weights and those measured in our laboratory with experimental samples. The latter figures are used in the subsequent calculations, because they more nearly reflect the state of polymers during melt density measurements. These values are consistent with those in our previous report[1].

Table 1 lists the Mark–Houwink constants used to calculate $\bar{M}_v$. The constants from refs 13 and 14 give essentially equivalent $\bar{M}_v$ values over the molecular weight range in which they were used. Mark–Houwink constants for low molecular weight polymers are reported to be independent of solvent and the nature of polymer end-groups[15], and the same values were used for toluene and benzene solutions.

The only specimens for which the molecular weight differed from the supplier's value to an extent which may be significant in the present context are polymers 11b and 12b. We have chosen to use our measured $\bar{M}_v$ figures because of the particular care with which these values were determined, as mentioned above.

An earlier publication[1] has directed attention to the fact that results of studies such as this will be critically dependent on the average molecular weights assigned to shorter chain polymers. Samples with the largest relative uncertainty in molecular weight are those which are richest in end-groups and in which the specific volume changes most with a given change in molecular weight. These are also the materials with the greatest influence on any data-fitting correlation, since they are at the extreme of the molecular weight range. The discrepancies reported here with samples 11b and 12b are in the measured intrinsic viscosities. Further uncertainties are involved in the assignment of $\bar{M}_v$ for a given intrinsic viscosity. This point, which cannot be resolved objectively at present, has been discussed elsewhere[1].

Many of the same anionic polystyrenes were used in a related study in which the main glass transition temperatures of anionic and thermally initiated polystyrenes were shown to be the same, at a given molecular weight[16]. The molecular weights of anionic polystyrenes used in that work were those reported by the supplier of these materials, since the specimens did not undergo the thermal history characteristic of the present melt volume study. The difference in assignment of molecular weight values to samples 11b and 12b does not affect the conclusion reached in the investigation of glass transition temperatures, since anionic and thermally initiated polymers fall into a common relation within experimental uncertainty regardless of the choices between these pairs of figures. This reflects the extent of scatter in reported glass transition temperatures of thermally initiated polystyrenes, in this instance.

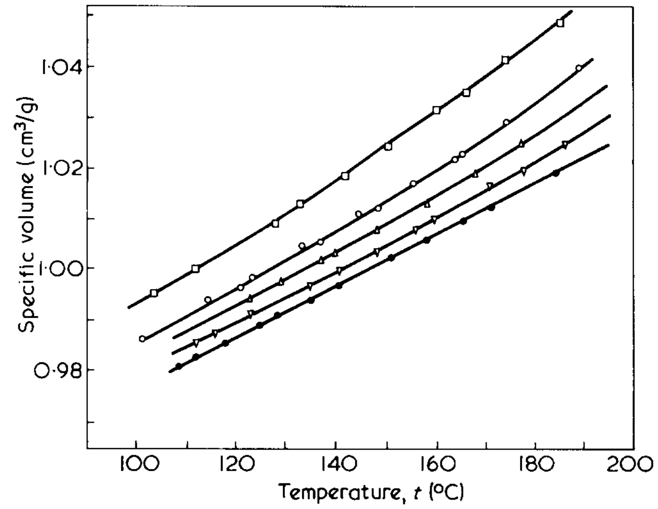

Figure 1 Specific volume vs. temperature from dilatometric measurements. Samples: □, 12b; ○, 11b; △, 8b; ▽, 2b; ●, 7b

RESULTS

The prime data from the static and flow melt density measurements have been reported earlier[1] and are not reproduced here. *Figure 1*[17] records the specific volume–temperature results for the five polystyrenes which were examined by dilatometry. Specific volumes at appropriate temperature intervals were read from the plots in *Figure 1*, to provide data at selected temperatures for subsequent analysis.

Temperatures for dilatometric measurements were between 101° and 193°C, but the extreme temperatures were not the same for all the polymers studied. The melt volume measurements were made in the range 170.1° to 237.0°C. To simplify the reduction of the results to a common relation we have interpolated the primary data to estimate molecular weight–specific volumes at eighteen temperatures between 110° and 237°C.

Melt volume data points for samples 7a and 4a at 237°C were discarded here, as in our first report[1] because of suspected leakage errors.

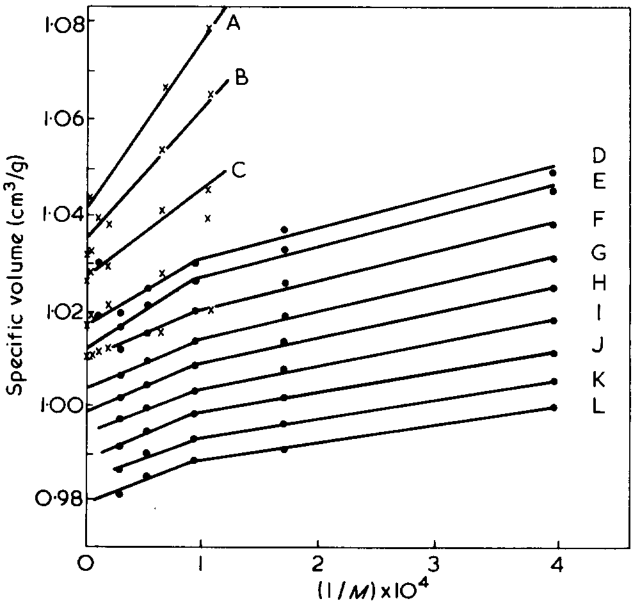

Figure 2 Specific volume–inverse molecular weight relations at temperatures (°C): A, 237; B, 217; C, 204.3; D, 186; E, 180; F, 170; G, 160; H, 150; I, 140; J, 130; K, 120; L, 110. ●, Dilatometric results; X, previous data from melt volume measurements[1]

We first compare the results of dilatometric measurements with those of the two newer techniques[7,8]. Sample 2b was used in dilatometry and sample 2a in static melt volume measurements[1]. Both polymers have similar molecular weights. The specific volume of polymer 2b was found to be 1.0169 cm^3/g at 170.1°C and that of sample 2a was 1.0158 cm^3/g at 170.0°C. The static melt volume value at 186.0°C was 1.0281 cm^3/g, while the dilatometric figure was 1.0261 cm^3/g. The latter value was calculated by interpolation between experimental points. The two sets of measurements agree to within 0.2%.

We have previously[1] shown that our measurements with sample 7a coincided with the dilatometric results of Höcker, Blake and Flory[18] at temperatures between 170° and 217°C, where both studies overlapped.

Figure 2 shows the observed specific volume–(molecular weight)$^{-1}$ relations at different temperatures between 110° and 237°C. These plots are shown as two intersecting straight lines, where the molecular weight range is large enough, because this fits the data and is in general agreement with the similar relations observed for thermally initiated polystyrenes[6]. A reasonable rectilinear fit could be obtained if the data points for the lowest molecular weight sample were discarded. The slopes and extrapolated intercepts on the ordinate of the low molecular weight regions of these plots are, however, more or less as predicted by the theory of Francois and coworkers[6] and the weight of evidence is shown below to indicate that the shapes of these plots are correct as shown.

The dilatometric results at 170.1°C and the data from the newer techniques coincide, as shown in *Figure 2*. A similar coincidence is shown at 186°C between experimental melt volume and interpolated dilatometry results. The curve shapes drawn in *Figure 2* are further supported by the data of Bender and Gaines[11] for low molecular weight, narrow distribution polymers. These values scatter about our dilatometric results. We conclude that the three experimental methods used to measure specific volumes all produce compatible results.

Our earlier data[1] were obtained with samples with molecular weights $\geqslant 9.4 \times 10^3$. All such specific volumes, including the newer dilatometric values, are linear in inverse molecular weight at fixed temperature.

Francois and coworkers[6] have recently re-examined the data of Fox and Flory[3] and Ueberreiter and Kanig[4] and have shown that the linearity of the isothermal specific volume–(molecular weight)$^{-1}$ relations for thermally initiated polytyrenes extends from high molecular weights only down to a molecular weight of about 10 000. A straight line with steeper slope and lower intercept accounts for the observations at molecular weights below 10 000. The same behaviour is noted in the present data for anionic polystyrenes. The rectilinear relations found earlier[1] for this polymer type are supported by the present data, but extension of these relations to lower molecular weights is evidently invalid, since our initial data included samples with molecular weights only as low as 9.4×10^3 where the bilinear relationship has an inflection.

The extrapolated intercept at $(1/M) = 0$ of our lower molecular weight data at 140°C is 0.999 cm^3/g. This is the same as the value plotted in Figure 5 of ref 6 for the low molecular weight data of Ueberreiter and Kanig[4] for free radical initiated polystyrenes. The slopes of the lines in the two cases differ, of course, because of the differences in end-groups.

DISCUSSION

The bilinear relationship shown in *Figure 2* between v and M^{-1} accounts for all the data points. It is probable that the true plot is curved, but we have an insufficient number of data points near the inflection region to draw curvilinear plots.

Table 2 lists the slopes and intercepts of the two straight line regions at each temperature in *Figure 1*. The tabulated values were obtained by linear least squares fits to the data points.

The v–M^{-1} data for $M \leqslant 10\,000$ with thermally initiated polystyrenes can be accounted for[6] by equation (1):

$$v = v_0 m + \frac{Me_1}{\bar{M}_n}(ve_1 - v_0 m) + \frac{Me_2}{\bar{M}_n}(ve_2 - v_0 m) \qquad (1)$$

Table 2 Slopes and intercepts of specific volume–M^{-1} plots

Temperature (°C)	$M \leqslant 10\,000$ Slope ($cm^3\,mol/g^2$)	Intercept (cm^3/g)	$M \geqslant 10\,000$ Slope ($cm^3\,mol/g^2$)	Intercept (cm^3/g)
110	37.6	0.984	93.8	0.979
120	38.7	0.989	94.2	0.984
125	39.2	0.992	94.7	0.987
130	41.7	0.994	97.7	0.989
135	44.5	0.997	100.8	0.991
140	47.1	0.999	97.9	0.994
145	50.1	1.001	96.7	0.997
150	51.9	1.004	101.7	0.999
155	53.9	1.007	104.5	1.002
160	55.9	1.009	108.4	1.004
165	57.3	1.012	115.8	1.006
170	57.7	1.016	97.2	1.010
175	58.7	1.019	136.7	1.011
180	58.9	1.022	145.7	1.013
186	59.2	1.026	160.3	1.018
204.3			182.7	1.027
217			313.1	1.033
237			363.2	1.042

Table 3 Slopes of v–M^{-1} plots for anionic polystyrenes with $M \leqslant 10\,000$

Temperature (°C)	v_0m (cm^3/g)	ve_1 (cm^3/g)	ve_2 (cm^3/g)	Calc. slope[a] (cm^3 mol/g^2)	Exp. slope (cm^3 mol/g^2)	Calc. slope[b] (cm^3 mol/g^2)	Calc. slope[c] (cm^3 mol/g^2)
110	0.984	1.596	1.047	41.4	37.6	38.8	44.6
120	0.989	1.618	1.053	42.4	38.7	39.8	45.8
125	0.992	1.630	1.055	42.9	39.2	40.2	46.3
130	0.994	1.641	1.058	43.5	41.7	40.8	47.0
135	0.997	1.653	1.061	44.0	44.5	41.2	47.6
140	0.999	1.664	1.064	44.6	47.1	41.8	48.3
145	1.001	1.676	1.067	45.3	50.1	42.4	49.0
150	1.004	1.689	1.070	45.8	51.9	42.9	49.6
155	1.007	1.701	1.073	46.4	53.9	43.3	50.2
160	1.009	1.714	1.076	47.1	55.9	44.0	51.0
165	1.072	1.726	1.079	47.6	57.3	44.4	51.6
170	1.016	1.739	1.082	48.0	57.7	44.8	52.1
175	1.019	1.753	1.084	48.6	58.7	45.3	52.8
180	1.022	1.766	1.087	49.2	58.9	45.8	53.5
186	1.026	1.782	1.091	49.8	59.2	46.4	54.2

[a] Using octane values in equation (2); [b] using nonane values in equation (2); [c] using heptane values in equation (2)

where v is the specific volume of polymer with number-average molecular weight $\bar{M}_n$, Me_i and ve_i are the molecular weight and specific volume of a specified chain end and v_0m is the extrapolated intercept of the low molecular weight region of the bilinear v–M^{-1}plot.

Francois and coworkers[6] have calculated the expected slopes of the low molecular weight regions of our plots at various temperatures by assuming that the anionic polystyrenes are capped with a butyl group and a styryl group. The partial specific volumes of such polystyrenes in solution were estimated reasonably well by assigning the butyl end a specific volume equal to that of octane[5], presumably to allow for the possibility that the attached polymer chain will restrict the freedom of movement of the alkane end. The same assumption was pursued by these authors in their estimation of specific volumes of bulk polystyrenes[6].

The slopes expected in the low molecular weight region of the v–M^{-1} plots are given by:

$$\text{Slope} = Me_1(ve_1 - v_0m) + Me_2(ve_2 - v_0m) \qquad (2)$$

The specific volume of the styryl end, ve_2, can be calculated[6] by assuming that ve_2 is 0.997 at 25°C and that the specific volume expansion coefficient, dv/dT, is equal to that of a low molecular weight polystyrene sample at 0.000581 cm^3/g K. The specific volumes of octane at the experimental temperatures are provided by Doolittle's correlation[19]:

$$\ln(ve_1) = \frac{a}{m} + b \qquad (3)$$

where

$$\ln a = 0.000275T + 2.303 \qquad (4)$$

$$b = 0.000182(T)^{1.19} \qquad (5)$$

and m is the molecular weight of the alkane molecule. For octyl and styryl end-groups, equation (2) becomes:

$$\text{Slope} = 57(ve_1 - v_0m) + 103(ve_2 - v_0m) \qquad (2a)$$

with the v_0m values obtained by linear least squares fits to the experimental data at the various temperatures.

Table 3 records v_0m, ve_1, ve_2 and calculated and experimental slopes. Calculated slopes differ slightly from those reported by Francois *et al.* for reasons which are not clear.

The estimated slopes in *Table 3* are certainly of the correct order of magnitude, although the experimental values are more sensitive to temperature than those predicted by this model. Use of the specific volume–temperature relation for nonane instead of octane in equation (3) produces a better fit at lower temperatures and more discrepancies between experimental and estimated slopes at higher temperatures. These calculated values are also listed in *Table 3*. Heptane specific volumes, which are also tabulated in *Table 3*, have the reverse effect.

The model used seems to be basically reasonable. The derivations between experimental and calculated values suggest that freedom of movement of the alkyl end of each polystyrene chain depends to some extent on the local viscosity of the attached polymer. At 110°C, for example, the v–M^{-1} slope with $M \leqslant 10\,000$ would be approximated by the behaviour of an isolated nonane or decane molecule. At 186°C the alkyl chain end is fitted by hexane or pentane behaviour. At somewhat higher temperatures, which are beyond our experimental range for the low molecular weight polystyrenes, one may expect that butane itself may provide the correct model for the then relatively unrestricted alkyl chain end.

The specific volumes of polystyrenes with $M \geqslant 10\,000$ are not entirely free of chain end effects, as might be expected. *Figure 3* compares high molecular weight data for anionic and thermally initiated polystyrenes at 170°, 186° and 217°C. Comparative data are relatively plentiful at these particular temperatures. The data of Fox and Flory[3] and Ueberreiter and Kanig[4] have been lumped together, although the end-groups of these thermally initiated fractions are not identical[6]. The straight lines in *Figure 3* are drawn subjectively through the scatter of data points and the slopes are not to be taken as definitive. It is clear, however, that the intercepts at infinite molecular weight are more or less equivalent for all polystyrene types, as may be expected, and that end-group volume contributions increase with decreasing molecular weight.

All polystyrene melts exhibit higher densities at higher molecular weights than would be predicted from the specific volumes of internal repeating units in lower molecular weight linear homologues. The striking analogy to partial

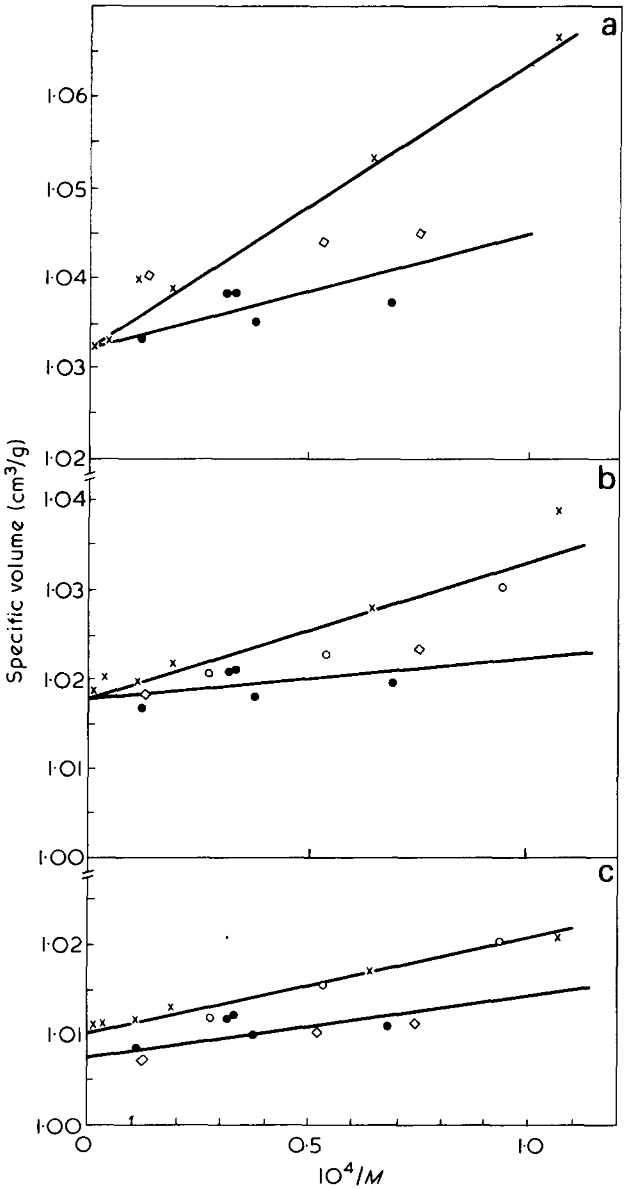

Figure 3 Specific volume–M^{-1} relations for thermally initiated and anionic polystyrenes. X, Present data from melt volume measurements[1]; ○, present dilatometric data; ●, data of Ueberreiter and Kanig[4]; ◇, data of Fox and Flory[3]. (a) 217°C; (b) 186°C; (c) 170°C

specific volumes in dilute solutions has been pointed out[6]. The latter phenomena fit an empirical relation between partial specific volume and segment density of the macromolecule. The factors which determine the dependence of partial specific volumes on molecular weight are presumably also important in bulk systems.

Our results are represented conveniently by two intersecting straight lines. We have, however, not tried to locate this intersection point accurately since the number of data points is insufficient to decide whether the relationship is not really a shallow curve. An apparent discontinuity is similarly reported for log–log Newtonian viscosity–molecular weight plots. Here again, a curvilinear relation may be closer to the truth[20,21] and we have therefore not tried to relate the apparent inflection points in the two sets of data.

ACKNOWLEDGEMENTS

The authors thank J. M. Hulme and Polysar Ltd for some of the molecular weight measurements and the National Research Council of Canada for financial support.

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