The Surface Tension of Poly(styrene)

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ABSTRACT: The surface tension of three anionically polymerized poly(styrenes) has been determined over the temperature range 100–225°, using the pendent drop method. Dilatometric density measurements over the same temperature range, and extending to below T_g, have also been performed. Blended samples have been studied to examine the effect of molecular weight distribution. In all cases, it is found that the surface tension at constant temperature is a linear function of $\bar{M}_n^{-2/3}$, as had been noted previously[1] for other polymers. These results are discussed in the light of available theoretical considerations, but it appears that our limited understanding of the bulk properties of polymer melts precludes any quantitative interpretation of the surface tension measurements.

Recent studies in this laboratory[1,2] have indicated that the surface tensions of liquid polymers, as well as those of other homologous series of organic chain compounds, obey relations of the form

$$\gamma = \gamma_\infty - \frac{k}{M^{2/3}} \qquad (1)$$

where M is the molecular weight and γ_∞ is the extrapolated infinite molecular weight surface tension. Such relations have been found to hold for the normal alkanes and perfluoroalkanes, poly(dimethylsiloxanes) and poly(isobutylenes),[1] and for certain poly(ethylene oxide) derivatives.[2] The availability of a series of narrow-distribution poly(styrenes) (prepared by anionic polymerization) has permitted us to investigate further the dependence of polymer surface tension on molecular weight and temperature, as well as to examine the question of the importance of molecular weight distribution on this property. We report here the results of this investigation, which may also be of some technical interest because of the practical importance of poly(styrene) as a thermoplastic. Because accurate density measurements are necessary for the surface tension determinations, and because we have been interested in a possible connection between surface tension and glass-transition temperature, dilatometric measurements over a wide temperature range have been performed and are reported.

Experimental Section

Materials. Three samples of poly(styrene) prepared by anionic polymerization,[3,4] in the molecular weight range 1000–10,000, were obtained from Arro Laboratories, Joliet, Ill. Characterization data obtained in this laboratory (Table I) were generally consistent with the supplier's specifications, although our $\bar{M}_n$ values are 10–15% lower. In our calculations, the values in Table I have been used. The samples were dried under vacuum and used without further purification. Infrared and nmr spectra of the three samples were identical, and conformed to those of poly(styrene); neither the ir nor nmr spectra permitted any characterization of end groups in these samples.

Blends were prepared by freeze-drying benzene solutions (*cf.* Table I). One blend (A) included a small amount of an anionically polymerized poly(styrene) of $\bar{M}_n$ = 97,600, obtained from Pressure Chemical Co., Pittsburgh, Pa. This material was used as received, without further characterization; the molecular weight value was that provided by the supplier.

Methods.[5] Absolute densities of the three narrow distribution poly(styrene) samples were measured at a single reference temperature with 1–2-ml pipet pycnometers,[6] and the variation of density with temperature was determined with conventional mercury dilatometers.[7] At temperatures well above T_g, equilibration times of 15–60 min were found adequate; near and below T_g, readings were made only after 8 hr or more at temperature. Densities of the glassy polymers at room temperature were determined by hydrostatic weighing.

Densities of the blended samples were calculated from their compositions; dilatometric measurements were performed on blend B, and the measured values agreed with those calculated within an average deviation of 5×10^{-4} g/cc.

Surface tensions were measured by the pendent drop method, as described by Roe.[8] Drops were formed on the tip of a glass syringe having a Teflon plunger. The syringe was mounted in a self-centering clamp, and calibration of magnification was accomplished by photographing a precision ball bearing mounted in the same clamp before and after each series of drop photographs. Temperature control in the pendent drop cell was maintained to ±0.1°, and absolute temperature values were checked by determining the melting points of several materials in the cell; these agreed with the cell thermocouple readings within ±0.2°. An argon atmosphere was maintained in the cell during all measurements. Photographs were made on Polaroid type 42 film, and measurements of the drop profiles were made with a travelling microscope reading to 10^{-3} cm. The measurement procedure recommended by Roe, Bacchetta, and Wong[9] was applied, and constancy of the calculated $1/H$ values to ±0.5% was accepted as a criterion of hydrodynamic equilibrium for each drop measured.

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[1] D. G. LeGrand and G. L. Gaines, Jr., *J. Colloid Interfac. Sci.*, **31**, 162 (1969).

[2] G. W. Bender, D. G. LeGrand, and G. L. Gaines, Jr., *Macromolecules*, **2**, 681 (1969).

[3] T. Altares, Jr., D. P. Wyman, and V. R. Allen, *J. Polym. Sci., Part A*, **2**, 4533 (1964).

[4] D. P. Wyman, L. J. Elyash, and W. J. Frazer, *J. Polym. Sci., Part A*, **3**, 681 (1965).

[5] A detailed account of our apparatus and procedures for density and surface tension measurements is available on request in GE R & D Center Report 69-C-228, G. W. Bender and G. L. Gaines, Jr. (1969).

[6] P. J. Flory, *J. Amer. Chem. Soc.*, **62**, 1057 (1940).

[7] N. Bekkedahl, *J. Res. Nat. Bur. Stand.*, **43**, 145 (1949).

[8] R.-J. Roe, *J. Phys. Chem.*, **72**, 2013 (1968).

[9] R.-J. Roe, V. L. Bacchetta, and P. M. G. Wong, *ibid.*, **71**, 4190 (1967). We are indebted to Dr. Roe for a copy of the tables referred to in this publication.

Table I
Properties of Poly(styrene) Samples

Sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g, deg: Measured: DSC[f]	Measured: Dilatometric[g]	Calcd: h	Calcd: i	Calcd: j
I	1680[a]	1.12[d]	48	51	41	56	40
II	2900[a]	1.12[d]	68	61 (67)	66	71	63
III	9290[b]	1.11[d,e]	86	94	89	87	88
A (I + 97,600)	1780[c]	3.93[c]					
B (I + III)	3030[c]	1.92[c]	62				
C (I + III)	8840[c]	1.04[c]					

[a] Vapor pressure osmometry in CCl_4. [b] Membrane osmometry in benzene. [c] Calculated from composition, assuming monodisperse components. [d] Gel permeation chromatography in benzene. [e] Ratio of $\bar{M}_w$ from light-scattering to $\bar{M}_n$ from osmometry agreed with value obtained by gpc. [f] Average of two to four runs, Perkin-Elmer DSC-1B instrument. [g] See Figure 1. [h] T. G Fox and P. J. Flory, *J. Polym. Sci.*, **14**, 315 (1954), eq III. [i] K. Ueberreiter and G. Kanig, *Z. Naturforsch.*, **6a**, 551 (1951), eq 1. [j] T. G Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955), eq 18-1.

Drop photographs were taken at intervals of 10–50 min after drop formation, and in no case was any significant change of surface tension with time observed. After completion of the measurements, the molecular weight of residual polymer from the syringe was redetermined by vapor pressure osmometry and gel permeation chromatography; no changes were detected. We believe, however, that the constancy of surface tension with time provides a more sensitive demonstration of the absence of degradative processes under the conditions used. Each reported surface tension measurement represents the average value from at least three photographs of two or more separate drops, which always agreed within ±0.3 dyn/cm.

Results and Discussion

Specific Volumes and Glass-Transition Temperatures. Figure 1 shows the specific volume–temperature relationships from the dilatometric measurements. The results of Fox and Flory[10] for a thermally polymerized poly(styrene) fraction having $\bar{M}_v$ = 1675 (the lowest molecular weight studied by them) are indicated by the dashed line. Above T_g, the specific volumes of the anionic polymers appear to be ~0.01 cm^3/g larger than those of the corresponding thermally polymerized fractions. Our data indicate a small change in slope of the volume–temperature line near 160°, although it is less pronounced than that observed by Fox and Flory.

Below T_g, our results show some discrepancies. For sample II ($\bar{M}_n$ = 2900), equilibration times of 8–12 hr were allowed, and it seems possible that the observed glass volumes may be high. For the other two samples, at least 20 hr at temperature elapsed before each measurement was recorded, and, we, therefore, have greater confidence that these results approximate equilibrium values. If it is assumed that the glass volumes obtained for samples I and III are also valid for II, the lower line on the figure should be used to estimate T_g, and a value of 61° is obtained for II. This procedure also receives support from the fact that this lower line corresponds in slope to the dv/dT values for glassy poly(styrene) obtained by previous workers.[10,11] It also extrapolates to a value of 0.959 cm^3/g at 23°, as compared to our measured values of 0.957 cm^3/g for sample II and 0.958 cm^3/g for III.

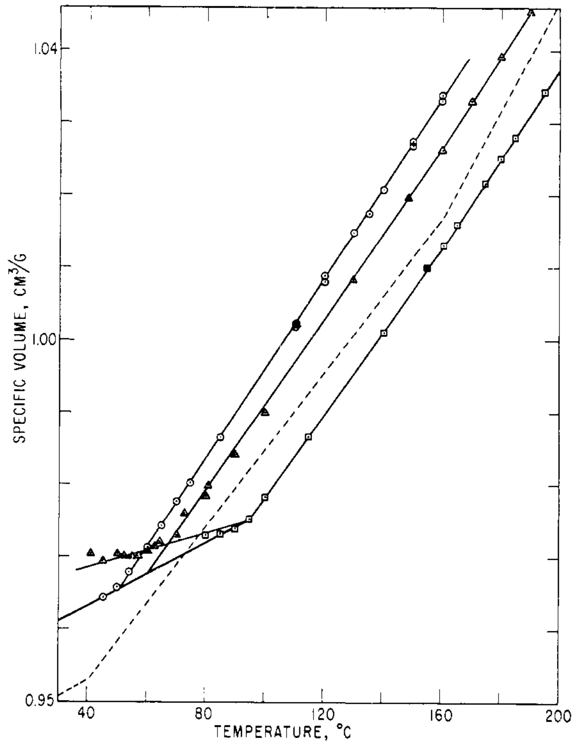

Figure 1. Specific volume *vs.* temperature for narrow-distribution poly(styrenes): ⊙, sample I, $\bar{M}_n$ = 1683; △, sample II, $\bar{M}_n$ = 2906; ⊡, sample III, $\bar{M}_n$ = 9290; dashed line, results of Fox and Flory for fractionated sample with $\bar{M}_v$ = 1675; solid points, reference measurements, determined pycnometrically.

On the other hand, if the dilatometric data for sample II below T_g are accepted, the upper line is appropriate. This leads to an estimate of T_g = 67° for this sample which is in better agreement with the DSC value (Table I). Any of the observed T_g values are in reasonable, although not exact, agreement with those calculated from equations generally believed applicable to low molecular weight poly(styrenes),[10–12] as noted in the table.

In any event, our results clearly indicate larger specific volumes for the glassy narrow distribution polymers than those reported for the thermally polymerized materials. Extrapolation of our volume–

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(10) (a) T. G Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950); (b) see Table I, footnote *h*.

(11) See Table I, footnote *i*.

(12) See Table I, footnote *j*.

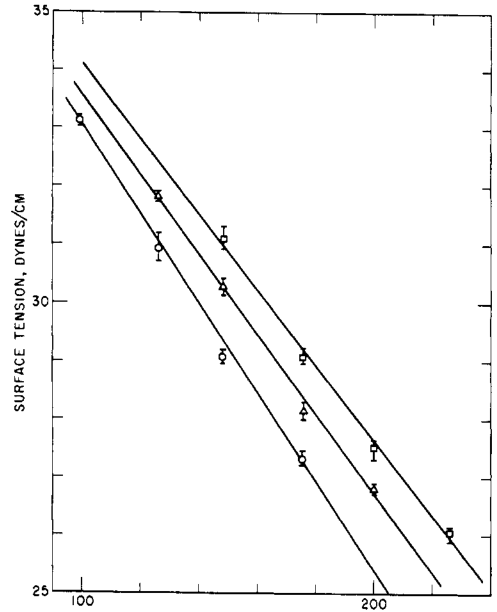

Figure 2. Surface tension of narrow-distribution poly-styrenes): ⊙, sample I, $\bar{M}_n$ = 1683; ◬, sample II, $\bar{M}_n$ = 2906; ⊡, sample III, $\bar{M}_n$ = 9290; error bars represent extremes of experimental observations; lines represent least-squares fits to averaged values.

temperature lines for the melts to the Fox and Flory line (Figure 1) would yield unreasonably low values of T_g (that for sample I would be 25°, whereas this sample is certainly still in the glassy state above room temperature). Whether this effect reflects the different end groups (presumably butyl, from butyllithium initiator (3)) in the anionically polymerized materials, or is related to the narrow molecular weight distribution, we are unable to determine.

Surface Tension. The temperature dependence of the surface tension of the three narrow-distribution poly(styrene) samples is shown in Figure 2. Least-squared lines through the average values at each temperature are shown. While some curvature in the γ–T plots cannot be ruled out, it appears that the data are consistent with constant $d\gamma/dT$ values over the range studied. It also appears that the magnitude of the temperature coefficient decreases slightly with increasing molecular weight; this effect, however, is barely outside experimental uncertainty and it is clearly not possible to assign any functional relationship. These results are also consistent with earlier measurements on commercial high molecular weight poly(styrenes); Harford and White[13] obtained γ = 28.0 dyn/cm at 200°, with $d\gamma/dT = -0.0586$ dyn/cm deg, while Oda and Hata[14] reported γ = 31.6 dyn/cm at 150°, and $d\gamma/dt = -0.071$ dyn/cm deg.

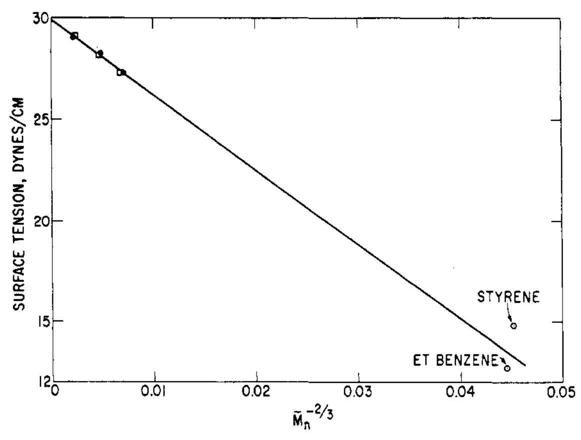

Figure 3. Molecular weight dependence of surface tension of poly(styrene) at 176°: ●, narrow-distribution samples; ⊡, blends (*cf.* Table I); ⊙, monomeric homologs (extrapolated values); straight line is based on values for narrow-distribution samples only.

In Figure 3, the measured surface tensions at 176° for the blended samples (Table I), as well as the narrow-distribution materials, are plotted *vs.* $\bar{M}_n^{-2/3}$. Points have also been included for styrene and ethylbenzene, which approximate the polymer repeat unit. These values have been obtained by extrapolation of measurements made below 100°,[15-17] and hence must be considered of very limited significance. Their correspondence with the plotted straight line, which is based on only the three measurements on the narrow distribution polymer samples, is encouraging nevertheless. A substantially similar plot would be obtained if number average molar volumes replaced $\bar{M}_n$'s. Since the present data permit no definitive choice between these related variables, we continue to accept the slightly better correlation with $\bar{M}_n$ for purposes of discussion.[1]

Clearly, the results for the blended samples fall on the same line, using $\bar{M}_n$ as the molecular weight parameter. While the experimental precision is not sufficient to be certain that there is not some slight deviation from the number-average, the weight-average molecular weight (or any higher moment) certainly would not fit. It is also worth noting that there does not appear to be any tendency for the lower molecular weight fraction to be strongly surface-active, since blends B and C exhibit surface tensions appropriate to their $\bar{M}_n$'s. Entirely similar results have been obtained for the blends over a range of temperatures similar to that covered for the narrow-distribution samples. There is, furthermore, no significant difference in the observed $d\gamma/dT$ values for the blends and the narrow-distribution samples of similar molecular weight. This suggests that, in this system at least, molecular weight distribution is not a significant factor in the observed low values of $d\gamma/dT$ as compared with simple nonpolymeric liquids, contrary to a suggestion made by one of us.[18]

Roe[19] has developed a corresponding states theory which appeared to correlate surface tension measurements for a few polymers with bulk properties. If we use the characteristic parameters tabulated by Roe for poly(styrene), the agreement of his theory with the present results is much less satisfactory. His theoretical curve leads to a predicted γ = 36.4 dyn/cm at 176°, while the experimental results shown in Figures 2 and 3

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(13) J. R. J. Harford and E. F. T. White, *Trans. J. Plastics Inst.*, 53 (Feb 1969).

(14) Y. Oda and T. Hata, paper presented at meeting of the Japanese Polymer Society, Tokyo, May 1968.

(15) D. R. Stull in "Styrene: Its Polymers, Copolymers, and Derivatives," R. H. Boundy and R. F. Boyer, Ed., Reinhold Publishing Corp., New York, N. Y., 1952, p 55.

(16) A. I. Vogel, *J. Chem. Soc.*, 607 (1948).

(17) O. R. Quayle, *J. Amer. Chem. Soc.*, **72**, 35 (1950).

(18) G. L. Gaines, Jr., *J. Phys. Chem.*, **73**, 3143 (1969).

(19) R.-J. Roe, *Proc. Nat. Acad. Sci. U. S.* **56**, 819 (1966).

are 27.3–29.1 dyn/cm, and the extrapolation to infinite molecular weight shown in Figure 3 yields a value of 29.9 dyn/cm at this temperature. A similar discrepancy appears at other temperatures, since Roe estimated a theoretical value of 45.9 dyn/cm at 20°, while linear extrapolation of our data to 20° yields 39.0–39.3 dyn/cm. (It should be emphasized that this extrapolated value, which refers to a hypothetical liquid state, is of doubtful significance.)

Roe[8] and Wu[20] have noted that MacLeod's exponent, *i.e.*, the slope of a log–log plot of surface tension *vs.* density, is lower for several polymers than the usual value (near 4) found for simple liquids. Their results for poly(isobutylene), however, indicated that this is not a general effect. The present results for poly(styrenes) are also consistent with a "normal" MacLeod's exponent (slopes of 3.8–4.1 are obtained depending on whether values for the various samples are plotted separately or all data are combined).

LeGrand and Gaines[1] attempted to relate the molecular weight dependence of surface tension to variations in glass transition temperatures by a crude free volume argument. Their expression for the slope of the γ *vs.* $M^{-2/3}$ plot was based on the premise (among others) that T_g is linearly related to $1/M$. This simple relation is not accurately obeyed by our materials. There is some uncertainty in the assignment of a $T_{g\infty}$, as well as the already noted difficulties with the T_g's of the experimental samples. Depending on these assignments, and which sample is considered, it is possible to calculate predicted slopes of 175–540, using eq 4 of ref 1. The slope of the line in Figure 3 is 366; because of the variation of $d\gamma/dT$ with molecular weight, the slopes at other temperatures would have somewhat different values, in the range 320–340. Hence we find, as before, that the results of this crude argument are qualitatively consistent with experiment, but cannot be used for quantitative correlation. The present results suggest that this difficulty is related at least as much to the qualitative nature of the free-volume relation for bulk properties as to our attempt to relate it to the surface tension.

Acknowledgment. We are indebted to D. G. LeGrand for many helpful discussions.

(20) S. Wu, *J. Colloid Interfac. Sci.*, 31, 153 (1969).

Separation by Flow

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ABSTRACT: Dilute solutions of finite size particles undergoing Brownian motion and flowing through a capillary have average velocities which depend on the particle size. Thus one can obtain a separation of particles of different sizes due to fluid flow. The elution volumes of suspended particles or polymer molecules are derived for various tube geometries. Following Taylor, the effects of diffusional broadening of the volume elution peak for finite size particles are discussed and a criteria for separation is given. It is found that particles very similar in size can always be separated. A scheme for separation by flow on a continuous basis is proposed.

I. Introduction

An isolated polymer molecule flowing down the inside of a thin capillary and undergoing Brownian motion will have an average velocity greater than that of the solvent. This is because the center of the particle (assumed to be a rigid sphere) cannot get any closer to the walls of the capillary than its radius. It therefore samples only those solvent velocities away from the walls. Since the solvent velocity is larger, the farther the distance from the wall, larger molecules will have larger average velocities than smaller molecules.

Suppose we now introduce particles of two different sizes simultaneously at the top of the column. The average distance between these particles will increase linearly with time as they flow through the tube because they have different average velocities. On the other hand the peak widths of the distribution of particle distances about their mean value for each kind of particle increases as the square root of time. This is a characteristic of particle diffusion. It therefore follows that by waiting for sufficiently long periods of time the separation between peaks can be made large compared to the width of the peaks. The particles therefore separate into two groups.

The purpose of this paper is to place the above ideas on a firm quantitative foundation.

Calculations of average velocity (and elution volume) of particles in right circular cylinders and parallel plates have been published.[1] Also, preliminary calculations showing the connection of the concept of separation by flow to gel permeation chromatography have been made.[2]

We will, in section IIA, derive formulas for the velocity of a polymer molecule as a function of both its size and the geometry of the tube through which it flows, as well as of its placement in the tube. The main conclusion of this section is that the velocity of the center of mass of a molecule in a general velocity field is approximately that which the fluid would have at the location occupied by the center of mass were the polymer molecule not there. In section IIB the average velocity and the elution volume in both circular cylinders and parallel plates are calculated. In IIC the dispersion in the elution volume peak due to diffusion and to the

(1) E. A. DiMarzio and C. M. Guttman, *J. Polym. Sci., Part B*, 7, 267 (1969).

(2) E. A. DiMarzio and C. M. Guttman, *Bull. Amer. Phys. Soc.*, **14**, 424 (1969).