NOTE

The Osmotic Behavior of Thermally Degraded Polystyrene

INTRODUCTION

In the process of studying the thermal degradation of polystyrene Grassie and Kerr[1-3] amassed a considerable amount of osmotic pressure data for thermally degraded polystyrene samples. They observed that after degradation the slopes of the π/C versus C curves for polystyrene in benzene at 25°C. increased beyond ca. 5% volatilization and quickly reached a maximum.[3] This maximum was the same for a range of parent polystyrenes of widely varying preparative histories. The π/C versus C curves were linear and the slope was equated to B, the second virial coefficient, from which the Flory-Huggins μ factor[4] was calculated. μ factors changed from ca. 0.428 for undegraded polymers to 0.328 for degraded samples. The original values of μ from ref. 3 have been recalculated in this work taking 1.105 for ρ (the partial density of polystyrene in benzene at 25°C.)[5] rather than 1.054—the bulk density of polystyrene. Grassie and Kerr interpreted this apparent decrease in μ as an increase in polymer–solvent interaction and suggested that it might be due to the disappearance of weak links during degradation.

In view of the support that this evidence rendered the much-disputed weak link theory[6] it was decided to re-examine the effect using an up-to-date osmometer.

EXPERIMENTAL

Polymers and Thermal Degradation

Polystyrene PS1 was prepared by polymerizing pure styrene monomer thermally in bulk at 42.5°C. in the absence of air to approx. 8% conversion. It was purified by the usual procedures but its molecular weight was too high to measure by osmometry. Polystyrenes HRM, beads and granules, were gifted by Shell Chemical Co.

Degradations were conducted in bulk at 320–330°C. in an apparatus described elsewhere.[1]

Osmometer and Membranes

A Mechrolab 501 High Speed Membrane Osmometer was used with gel cellophane membranes 300 grade (kindly supplied by Dr. N. Grassie) and Ultracellafilters "allerfeinst" grade. "Analar" benzene was used as solvent and the temperature was 25°C.

The undegraded polymers showed no diffusion through the membranes but degraded samples diffused to some extent, particularly with the 300 grade membranes, and osmotic heads were obtained by extrapolation to zero time. With the 501 Osmometer this procedure is less prone to errors than with older instruments due to its high sensitivity and rapidity in operation (an osmotic pressure measurement can be made in 10–18 min.).

RESULTS AND DISCUSSION

Typical results of osmotic pressure measurements are shown in Figure 1 which includes data for both undegraded and degraded samples, including, for comparison, a curve computed from Grassie and Kerr's data. Table I summarizes μ values from the present and other relevant sources.

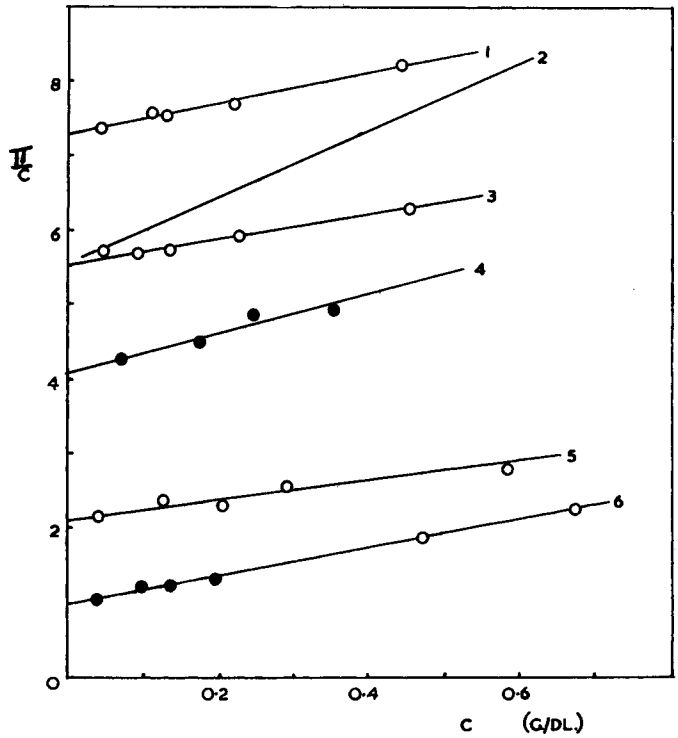

Fig. 1. π/C versus C curves for polystyrene in benzene solution at 25°C. (O) with allerfeinst membrane; (●) with 300 grade membrane. Extents of volatilization: (*1*) PS1: 22; (*2*) slope from ref. 3; (*3*) PS1 16; (*4*) PS1 9.5; (*5*) Polystyrene HRM (Granules) (O); (*6*) Polystyrene HRM (Beads) (O).

With the possible exception of curve 4, Figure 1, all five samples examined have very similar μ values—probably the same within experimental error. This observation contradicts the results previously recorded,[3] and an adequate explanation for this disparity is not hard to seek. In the first place it is significant that the only substantial difference in the present and previous results is the sensitivity of the osmometers to diffusible species. Grassie and coworkers[3,7] used a Fuoss-Mead type osmometer with a bacterial cellulose membrane which for most degraded samples allowed some diffusion. This is hardly surprising since the nature of polystyrene pyrolysis is such that the production of some low polymer is inevitable. It would seem that the apparent decrease in μ after degradation is really some effect of a "leaky" membrane and not a genuine increase in polymer–solvent interaction. Other results support this view.

Firstly, as Table I shows, later work[7] with the Fuoss-Mead osmometer at 30°C. and the same membrane revealed an even more striking decrease in μ which could hardly be attributed to increasing polymer–solvent interaction with increasing temperature since μ is not very temperature sensitive. On the other hand, this change in temperature could conceivably increase polymer diffusion. Secondly, it was found in the same work[7] that if the degraded polystyrene sample was dissolved in benzene, precipitated in methanol, and dried and redissolved in benzene the μ factor increased again, though never quite to the value for the undegraded samples (see Table I). It is more than likely that this treatment removes some of the smaller polymer fragments.[8] Finally, Meyerhoff, Donnet, and Roth[8] found that the experimental value of the second virial

TABLE I
μ Factors for Polystyrene in Benzene

Sample treatment	Osmometer temperature, °C.	μ	Reference
Thermal degradation	25	0.312	7
Thermal degradation	25	0.328	3
Thermal degradation	30	0.165	7
Thermal degradation and precipitation	25	0.362	7
Thermal degradation and precipitation	30	0.267	7
Thermal degradation (9.5%)	25	0.400	Present
Thermal degradation (16%)	25	0.442	Present
Thermal degradation (22%)	25	0.421	Present
Undegraded S.7	25	0.428	3
Undegraded S.7	30	0.410	7
Undegraded	31.5	0.467	9
Undegraded HRM (granules)	25	0.453	Present
Undegraded HRM (beads)	25	0.427	Present

coefficient for polydisperse polystyrene increases with the amount of low polymer capable of leaking through the membrane. These authors suggest that the apparent increase in B (or decrease in μ) arises from a small amount of polymer diffusing through the membrane at low concentrations, thus greatly diminishing π/C, while at higher concentrations the proportional variation cannot occur because of the far greater amount of diffusion required. The net result is that the gradient of the curve $\pi/C = f(C)$ is exaggerated, giving an irregularly high value for B. It is also noteworthy that the sample which showed the most diffusion in the present work (Fig. 1 curve 4) shows the lowest value of μ.

In conclusion, it seems more reasonable to suppose that the diminished μ values for degraded polystyrenes previously reported[3] were a direct result of a leaking osmometer membrane and were not due to any significant increase in polymer–solvent interaction. Thus, far from supporting the weak link theory of polystyrene degradation, this communication casts doubts on it, for it suggests not only that the change in μ on degradation has nothing to do with weak links, but that osmotically determined molecular weights of degraded polystyrenes are unreliably high. Accordingly, conclusions based on them may have to be revised.

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