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THERMAL ANALYSES OF POLYMERS. X. CALORIMETRIC AND LIGHT TRANSMISSION CHARACTERISTICS OF MONODISPERSE POLYSTYRENES

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ABSTRACT

The techniques of differential scanning calorimetry (DSC), thermal depolarization analysis, and white light transmission *vs.* temperature, have been used to study the thermal characteristics of a series of monodisperse polystyrenes. Low molecular weight polystyrene oligomers whose molecular weights are less than 10,000 show first-order fusion phenomena by all three techniques. Those polymers of 20,000 molecular weight or higher exhibit what has been observed as the normal response for high molecular weight polystyrene. Changes that occur in the DSC characteristics for the low molecular weight oligomers manifest themselves as abrupt changes in depolarized light, significant of first-order fusion phenomena. A plot of the temperature changes *vs.* molecular weight, for the three experimental methods used in this study, showed the same type of asymptotic relationship observed by Fox and Flory[1], at molecular weights of 10,000 and above. Measurements of depolarized light show an increase in transmission as a function of molecular weight, even at molecular weights above 10,000, whereas white light transmission characteristics point to the occurrence of two discrete melting phenomena occurring above molecular weights of 10,000. A plot of $1/\overline{M}_n$ *vs.* T shows an inflection for two different linear relationships near a molecular weight of 5,000, in good agreement with previously reported data.

INTRODUCTION

While most of the physical property studies about polystyrene deal with bulk samples of varying molecular weight distribution, only a small number of measurements have been made with well-characterized fractions. The original and classical work of Fox and Flory[1] showed that with the use of well-characterized fractions, an asymptotic relationship between molecular weight and specific volume occurred over the molecular weight interval to 100,000. Similarly, a plot of the specific volume *vs.* reciprocal molecular weight yielded a linear relationship. Intrinsic viscosity relationships were also developed to show the same types of correlation[2]. Beevers and White[3] have shown the same asymptotic relationship between the glass transition and number average molecular weight for polymethylmethacrylate, as that of Fox and Flory for polystyrene.

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With the commercial availability of monodisperse polystyrenes, Connor[4] was able to examine a broad series of varying molecular weight polystyrenes from 900 to 1.8×10^6 by nuclear magnetic resonance techniques. His results have shown that the major T_g region or α-transition was influenced by the low temperature γ-transition, in the form of a relaxation which occurred on the low temperature side of the α-transition. This variation in temperature of the α-transition was clearly indicated by the non-exponential character of dielectric, mechanical, and NMR data.

However, recently, Jentoft and Gouw[5] were able to separate a monodisperse polystyrene sample of molecular weight 600, from the Pressure Chemical Company, into approximately eighteen oligomers by means of supercritical fluid chromatography, raising some question of the nature of the PS fractions. Nonetheless, they are the only samples of commercial origin which show a monodisperse distribution by accepted techniques.

This paper reports the differential scanning calorimetric and light transmission response of monodisperse polystyrenes of varying molecular weight, to show the influence of molecular weight of monodisperse polymer on the α-transition, agreeing with the early results of Fox and Flory, as well as to illustrate complete lack of molecular order of only the high molecular weight polystyrene fractions.

EXPERIMENTAL

The polystyrene samples used in this study were obtained from the Pressure Chemical Company. All the samples were reported to have a polydispersity in the range 1.1 ± 0.1.

The DSC characteristics were determined on a DuPont 900 Thermal Analyzer at a heating rate of 10°C per min, and the thermal depolarization analyses (TDA) and white light characteristics were measured as previously described at a heating rate of 5°C per min[6,7].

RESULTS

The polystyrene fractions used in this work were reported to be anionically prepared by initiation with *n*-butyl lithium, and termination and precipitation were accomplished by the addition of methanol. Hence, the chains have *n*-butyl groups on the initiating ends and methoxy groups on the terminating ends.

The thermal characteristics of a 1.8×10^6 molecular weight polystyrene are shown in Fig. 1, wherein the DSC scan showed the normal endothermal response at 109°C without accompanying transitions or changes. The TDA curve in Fig. 1 showed a probable change around 110°C, and some fusion or molecular disordering occurring at 220°C and 249°C.

TDA is the measure of the change in birefringence with temperature, and may be affected by form birefringence and scattering, though these are usually minor factors. Usually TDA results indicate an increase in molecular order as the light transmission value increases and a fusion or decrease in molecular order as the light

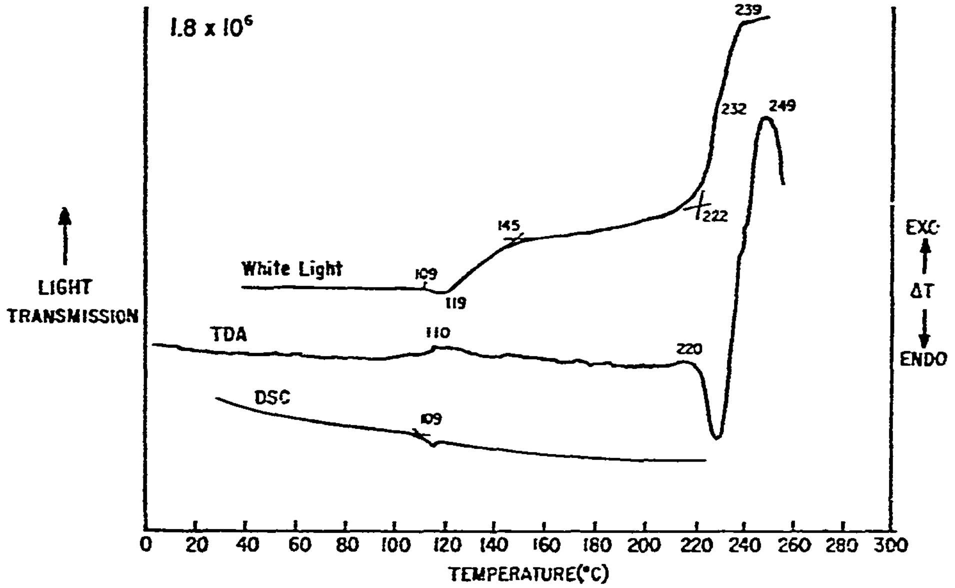

Fig. 1. DSC, TDA, and turbidity behavior of polystyrene ($M = 1.8 \times 10^6$).

intensity decreases. Contrarily, white light transmission increases as molecular disorder or fusion occurs[6,7].

The white light characteristics confirm the character of the TDA response, as the white light curve began to decrease at 109°C followed by an increase at 119°C. While the rate of change above 145°C is decreased an increase was apparent at 222°C,

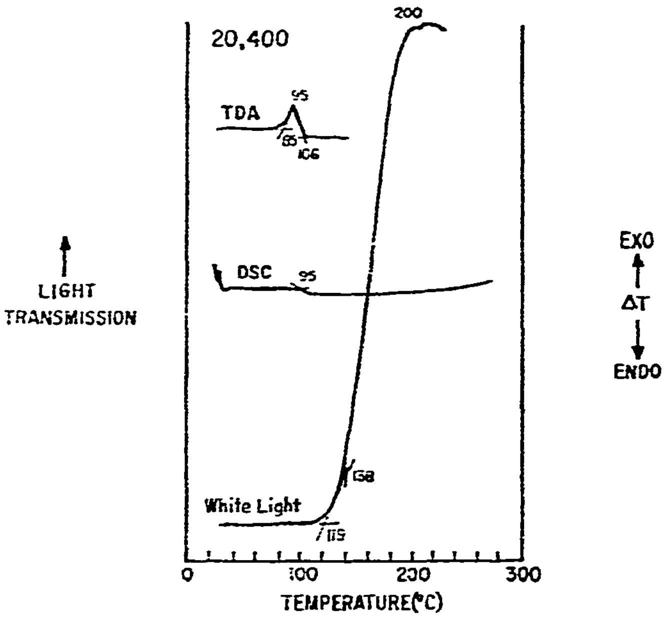

Fig. 2. DSC, TDA, and turbidity behavior of polystyrene ($M = 20{,}400$).

followed by complete transmission at 239°C. An intermediate jog or knee occurred at 232°C during the fusion process. The occurrence of the large increase in transmission between 222°C and 239°C for white light, as well as the decrease in depolarization at 220°C, confirmed the fact that the sample, as received, began to melt near 220°C, with final fusion occurring near 249°C.

When the sample was rerun by TDA, there was no response over the temperature range shown in Fig. 1, since all of the molecular order induced by the precipitation process in the preparation of the polymer had been melted out in the first run. The DSC response, when rerunning the sample, was identical to the first run. White light characteristics on rerunning showed no changes until 220°C, where an increase in light transmission began, with the highest transmission level accomplished at 239°C, similar to the first determination. Polystyrene samples of molecular weight 670,000 and 498,000 behaved very similarly to the 1.8×10^6 molecular weight sample.

In Fig. 2 are shown the DSC, TDA, and white light characteristics for 20,400 molecular weight polystyrene. The DSC response illustrated a heat capacity change at 95°C, and the depolarization scan showed the onset of molecular motion at 85°C with a peak at 95°C, followed by terminal fusion at 106°C. The white light characteristics traced the onset of decreasing turbidity at 119°C, with final clarity achieved at 200°C. A rerun of each of these techniques showed the DSC to be identical in its behavior, whereas the TDA response merely reflected a decreasing step change occurring at an extrapolated onset of 95°C, followed by zero light transmission or terminal fusion at 115°C.

For the rerun, there was no peak, and the change in depolarization level began to decrease as low as 60°C. This type of TDA response on reheating was found to be

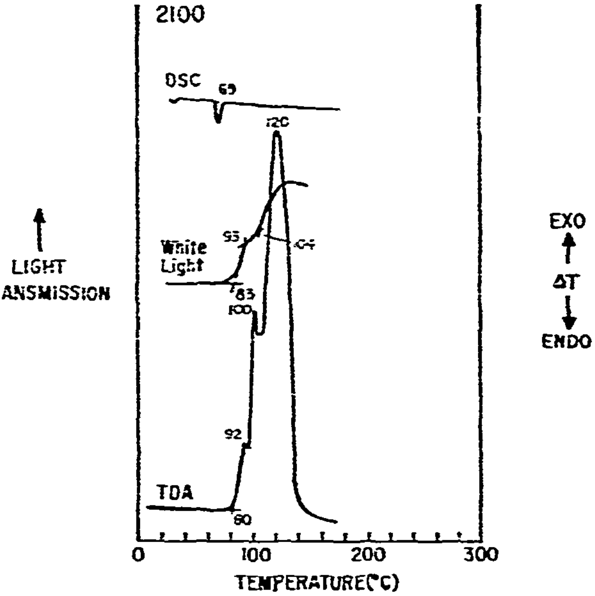

Fig. 3. DSC, TDA, and turbidity behavior of polystyrene ($M = 2{,}100$).

typical of a 200,000 molecular weight polystyrene sample. When a monodisperse polystyrene of a molecular weight between 20,000 and 200,000 molecular weight was compression-molded, and cooled under a proper temperature program, a totally different morphological influence was seen in the thermal diagrams. The inferences derived from thermal history will be reported in a later publication[8].

In Fig. 3 are shown the DSC, white light, and TDA characteristics of a 2,100 molecular weight fraction of polystyrene. The DSC endotherm occurred sharply at 69°C; the TDA curve, on the other hand, showed changes beginning at 80°C with peaks at 92°, 100°, and 120°C, prior to final fusion at 140°C. The white light characteristics confirmed the changes in TDA near 83°, 93°, and 140°C, at which point the polystyrene was completely transparent. Rerunning this sample after slowly cooling produced similar results to those shown in Fig. 3.

Molecular ordering has been observed by X-ray diffraction for polystyrenes of narrow molecular weight distribution which are oligomeric liquids at room temperature. The existence of a smectic phase of short and rigid polystyrene oligomers which are arranged parallel to one another, has been suggested as the cause of the molecular ordering[9]. In Fig. 4 we see the thermal response of a 600-molecular weight oligomeric polystyrene in which the DSC showed a heat capacity change at −16 °C. The TDA characteristics show an increase in molecular ordering at −48 °C, followed by the onset of fusion at −18°C, with final fusion at 5°C. The white light character-, istics confirmed the changes in the TDA scan with a decrease in turbidity at −36 °C followed by further decreases at −18 °C and −8 °C. There was an apparent increase in turbidity from −3° to 5 °C, followed by a very rapid clarification, between 5° and 15°C, of the polystyrene melt. On rerunning these materials, after cooling at reason-

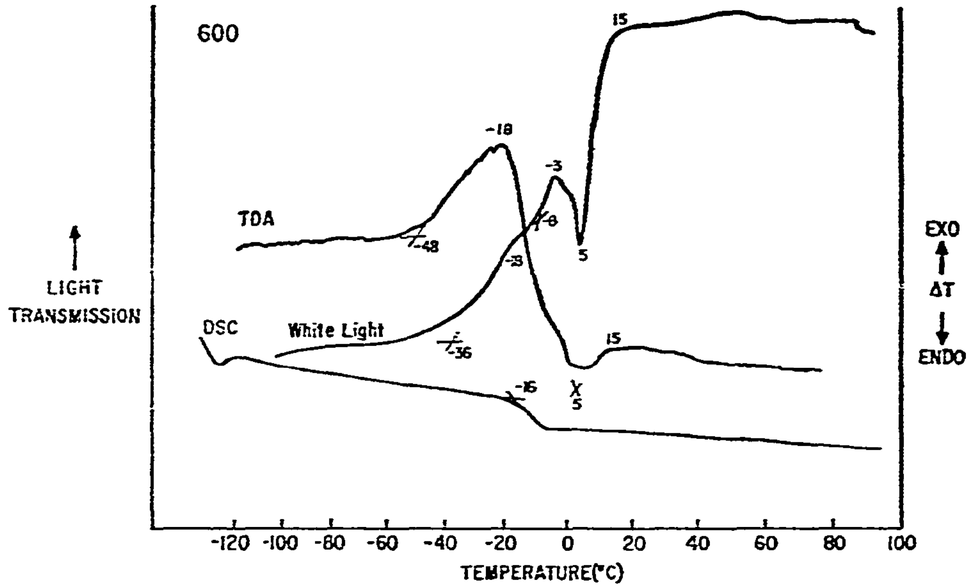

Fig. 4. DSC, TDA, and turbidity behavior of polystyrene ($M = 600$).

able rates, the results were identical. These results tend to support the data of Morimoto[9] in that low molecular weight polystyrenes exhibit some degree of molecular ordering, even at molecular weights as low as 600.

DISCUSSION

The shaded area in Fig. 5 encompasses the temperature *vs.* molecular weight band, into which the measurements fall by DSC (○), TDA (⊙), and the beginning of white light changes (×), and these data are in good agreement with the dilatometric

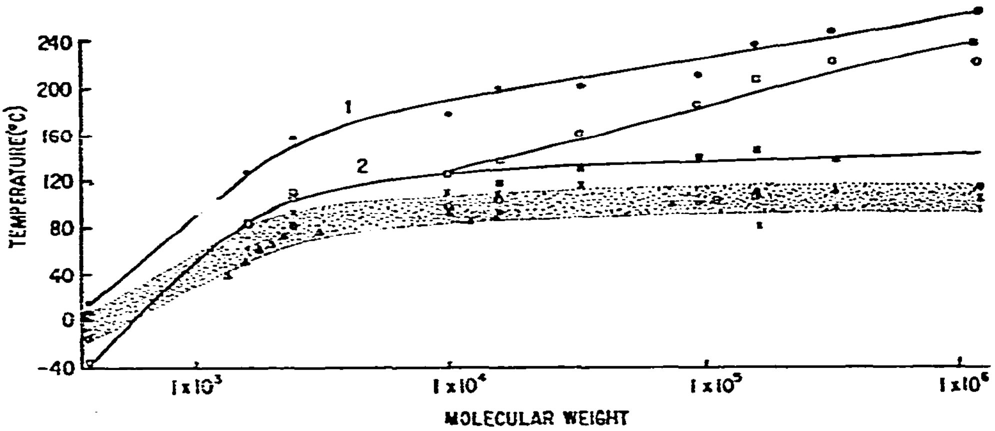

Fig. 5. Molecular weight relationships by DSC (○), TDA (⊙), White Light Transmission [beginning (×); curve 2, extrapolated onset (□, ■); curve 1, final melt (●)] and Dilatometry (△) (Ref. 1).

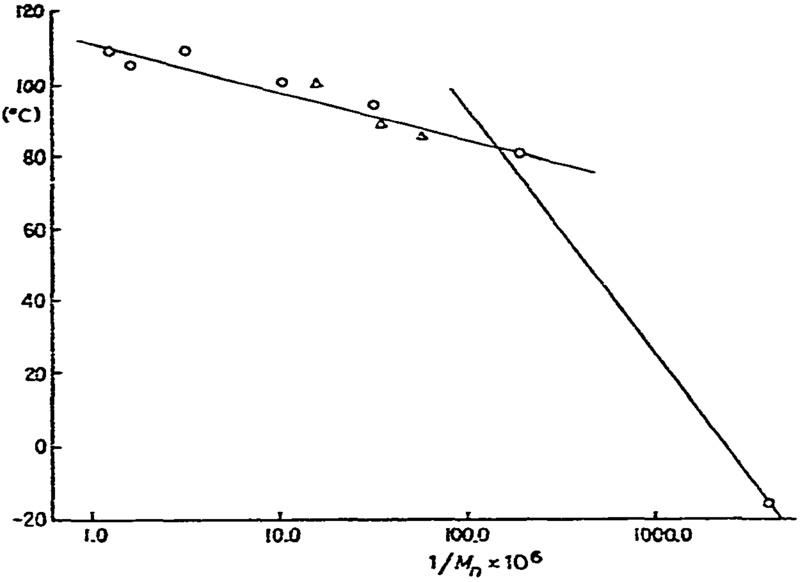

Fig. 6. Log M_n^{-1} *vs.* Temperature [DSC (○); Fox and Flory[1] (△)].

data (△) of Fox and Flory[1]. The extrapolated onset of changes in white light transmission (□ and ■ in Fig. 5, curve 2) show that above molecular weights of 10,000, two changes occur in the light transmission. Apparently, the onset temperature increases asymptotically, and it normally would level off. However, a second change in light transmission at a lower temperature (■) occurs above molecular weight, $M = 10{,}000$, and its rate of change increases linearly to 120°C. The final melt (●) (Fig. 5, curve 1) as observed by turbidity measurements, increases linearly in the same manner as the onset of changes in white light from $M = 5{,}000$ to 1.8×10^6. Hence, there is good agreement between dilatometric, viscosity, differential scanning calorimetry, light transmission, and thermal depolarization data for determining the molecular weight dependence of a transition temperature.

TABLE I

MOLECULAR WEIGHTS AND TRANSITION TEMPERATURES OF POLYSTYRENE FRACTIONS

M_w	$M_w^{-1} \times 10^6$	*Dilatometry*[1] (°C)	*DSC* (°C)
600	16,000		−16
1,675	5,900	40	
2,100	4,800	53	69
2,600	3,840	62	
3,000	3,330	65	
3,600	2,770	75	
4,000	2,500		81
5,000	2,000	78	
10,000	1,000		93
13,300	750	86	
19,300	520	89	
20,400	498		93
85,000	110	100	
97,200	103		100
200,000	50		109
498,000	20		105
670,000	14		111
1.8×10^6	5		109

The data in Fig. 6 and Table I show the excellent linear correlation between the log of the reciprocal weight average molecular weight and the transition temperature observed by DSC in this work, and by dilatometry in the work of Fox and Flory[1]. A definite change in slope is perceivable below a molecular weight of about 6,000. The plot of the log melt viscosity *vs.* log molecular weight by Fox and Flory[2] showed an intersection of two straight lines in the molecular weight region of 38,000 with a tailing curvature beginning near a molecular weight of 6,000. This curvature and tailing of the log viscosity plot of Fox and Flory is almost superimposable with the change in slope in the transition temperature–log M^{-1}, in this work below 10,000. The change in slope above 38,000 for the log viscosity–log molecular weight plot of

Fox and Flory is manifested as a change in the white light intensity in that molecular weight region from this work (Fig. 5, curve 2). These results suggest the relationship of log M *vs.* T or log M^{-1} *vs.* T rather than the linear correlation, over a very small molecular weight range[1,2].

The influence of thermal history on the TDA characteristics of polystyrene behavior is similar to that observed by DTA, DSC or dilatometry. Slow cooling will often produce a curve which exhibits a peak just prior to fusion, whereas rapid quenching will produce a smooth step in the curve. The beginning of melting or change can usually be followed by the onset of departure from the linearity of the trace. The temperature of fusion will be more accurate when taken as the extrapolated onset of the decrease in transmission at reasonable heating rates. At slower heating rates, the attainment of the isotropic state will probably be coincident with final fusion.

The peak in the TDA trace is usually the result of the beginning of melting, with a decrease in scattering from the surface of the powder particles. An increase in transmission also occurs when the particles coalesce during the initial stages of melting, raising the birefringence. Lastly, a peak can be present if only one cover slip is used in the measurement, for scattering from the surface of the sample will occur as the physical topography of the sample changes during melting or during the relaxation of the polymer. These traits are obvious when viewed with a polarizing microscope.

The techniques of differential scanning calorimetry, thermal depolarization analysis, and white light transmission enable one to readily assess the molecular weight dependence of the basic properties of the polymer. Polystyrenes used in this work are apparently completely atactic for molecular weights only above 200,000 since they show no TDA response on reheating, whereas those below 200,000 show repeatable changes in birefringence similar to the melting of crystalline monomers[6].

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