Since the change in crystallinity is negligible, the transition zone in the mechanical properties vs. temperature results obtained by means of a Clash-Berg tester reflects mainly the increase of the chain mobility of the amorphous phase of the polymer. Thus, from a phenomenological point of view, the temperature obtained by the Tobolsky method is essentially equivalent to that obtained by the dilatometric method. In fact by the latter procedure[10] the T_g was found to be 50 °C, whereas in Figure 1 $T_1(10) = 54$ °C is in good agreement with the above result. Moreover the measurements given by the dilatometric method are not influenced by the previous thermal history of the samples as well.

In conclusion, it seems that dilatometric or mechanical measurements on Nylon 6 give the glass transition temperature in its classical meaning, without any of the troubles that seem to arise from measurements based on variations in thermal properties.

On the other hand, as discussed by Gordon[7] the peak observed on heating in DTA or DSC measurements can be due to the breaking of some of the hydrogen bonds present in the amorphous phase that cannot reform in time during the subsequent cooling. The results shown in this work are in agreement with the Gordon interpretation. In fact it is possible that the presence of a high percentage of crystallinity makes the variation in the thermal dependence of the mechanical properties of the amorphous fraction so small that it cannot be detected because of the low sensitivity of the apparatus.

Also the effect of crystallinity is detectable in dilatometric measurements,[10] where the ratio between the slopes above and below T_g is only about 1.5. That is a lower value with respect to those obtained for completely amorphous polymers.[9b]

In the DTA or DSC experiments, according to our interpretation, one would detect therefore only the phenomenon suggested by Gordon in his paper. But this mechanism does not seem to be the main cause of the increase in the chain mobility usually invoked to describe the transition zone between the glassy and rubbery states, since there is an absence of anomalous behavior in dilatometric and mechanical experiments.

Furthermore, as reported by Gordon, the peak of the DTA or DSC measurements does not appear at the same temperature because of its dependence on the thermal history of the samples and this again is reasonably explained through the delay in reforming of hydrogen bonds in the amorphous phase.

A final remark concerns the eventual presence of multiple glass transition temperatures as reported by Boyer[11] for other semicrystalline polymers. This is related to the nature of what we have called the "amorphous phase", which may not be considered perfectly distinguishable from the crystalline phase. That is, between the two phases an intermediate structure can be present, the relative amount of which increases with increasing degree of crystallinity. It seems to us that the Tobolsky method cannot resolve the different glass transitions connected with the motions of the various types of macromolecules interacting with the crystalline phase. But this situation can affect the measured $T_i(10)$ at increasing crystallinity, and on this point more experimental study is planned.

However, the isochronal curve representing modulus-temperature results also gives for a semicrystalline polymer an easy way of determining the phenomenological glass transition temperature besides the levels of the glassy and rubbery plateaus which could be very useful from the technical point of view.

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The Dimensions of Polystyrene Near and Below the Theta Temperature

E. SLAGOWSKI, B. TSAI, and D. McINTYRE*

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

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In the course of examining the behavior of extremely high molecular weight polystyrenes[1,2] it seemed worthwhile to examine the behavior of the highest molecular weight sample near the theta temperature. Stockmayer[3] had earlier suggested that the collapse of a coil might occur near the theta temperature. However, viscosity measurements near the theta temperature with the commonly available polystyrene samples had shown no particularly dramatic effect. It is the purpose of this note to show that the radius of gyration of an extremely high molecular weight polystyrene fraction measured by light scattering does show a rapid decrease just below the theta temperature. An analysis of the asymptotic behavior of the scattering curves for this same system in the same temperature range has recently been published[4] and the theoretical implications are extensively discussed there.

A sample of polystyrene anionically polymerized as discussed in ref 1 and 2 was examined by light scattering and equilibrium centrifugation in cyclohexane solutions. The light scattering photometer was designed to measure down to 12° (angle) and the cell was thermostated to ±0.05 °C.

The weight-average molecular weight determined by the light-scattering method at the theta temperature based on calibration with standard NBS sample 705 was 44.4 × 10^6 g/mol. The weight-average molecular weight determined by equilibrium sedimentation using a Spinco Model E at 800 rpm was 43.5 × 10^6 g/mol. The z-average molecular weight was also measured by sedimentation analysis and found to be 48.8 so that the polydispersity (M_z/M_w) of the sample is known to be low (ca. 1:1). Furthermore the molecular weight is known to

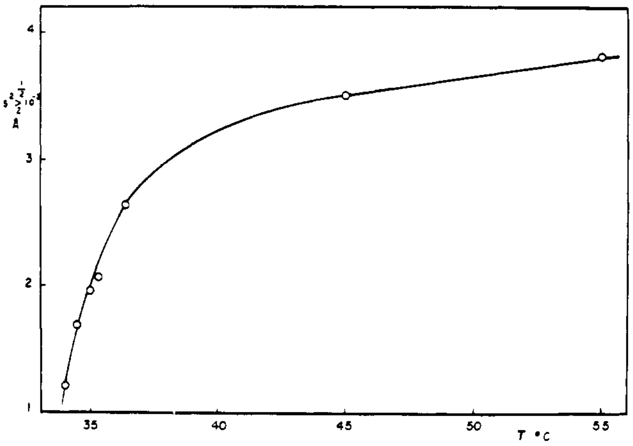

Figure 1. Phase diagram of polystyrene (4.4 × 10^7 mol wt).

Table I
Virial Coefficients and Expansion Factors as a Function of Temperature

t, °C	$A_2 \times 10^5$, (g^2 cm^3)/mol	α^2
34	−9.8	0.341
34.5	−4.1	0.675
35	−2.73	0.908
35.4	0	1.0
36.4	0.29	1.36
45	1.64	2.39
55	3.38	2.82

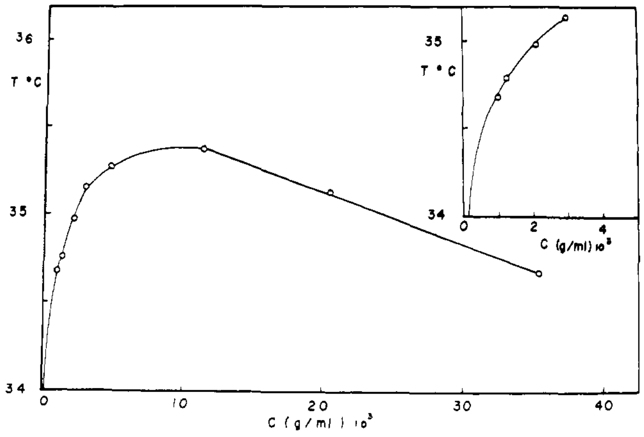

Figure 2. Radius of gyration.

be accurate within approximately 2%.

The phase diagram for this sample was measured and is shown in Figure 1. The critical temperature of this sample was taken to be the maximum in the phase diagram and is 35.4 ± 0.05 °C at a concentration near 1 g/dl. Therefore, the critical temperature is at the theta temperature determined by light scattering. Thus there are no deviations at high molecular weight from the concept of the theta temperature being simultaneously the critical miscibility temperature of an infinite molecular weight sample and the temperature at which the second virial coefficient is zero (see Table I). The critical temperature is in excellent agreement with the linear relation T_c^{-1} vs. $M^{-1/2}$ eablished from lower molecular weight samples[5] and is therefore convincing experimental proof of Casassa's recent comments concerning limiting critical behavior.[6] The light scattering measurements were made at concentrations two to almost three orders of magnitude below the critical concentration, i.e., at 0.02 to 0.002 g/dl. Therefore the solutions used in the light-scattering measurements should phase separate only below 34 °C. Visual observation and photometric scanning confirm the fact that these dilute solutions were not phase separated at 34 °C, the lowest temperature used for the light-scattering measurements.

The z-average radius of gyration of the theta temperature is 2070 Å and Table I lists the values of α^2 the chain expansion factor, where $\alpha^2 = \langle S^2 \rangle / \langle S^2 \rangle_\Theta$, as well as the virial coefficient. Figure 2 illustrates the dramatic change of the radius as the temperature is lowered from slightly above to slightly below the theta temperature. Even though the temperature changes uniformly in half-degree increments from 35.5 to 34.0 °C, α decreases by an increasing factor. Of course, the lowest value of α is 0.58 which is an order of magnitude larger than the collapse into a sphere containing densely packed segments. Since the virial coefficient is becoming negative at an accelerating rate at this low α, it is unlikely that the single collapsed coil can exist before phase separation begins. However, these data indicate that a polymer coil can be brought to about half its unperturbed size before there is separation into two phases. Further experiments are in progress to determine the nature of high molecular weight polymer coils in this contracted state.

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Chemical Modification of Polymers. 9. Attack of Nitrogen Anions on Poly(vinylbenzyl chloride)

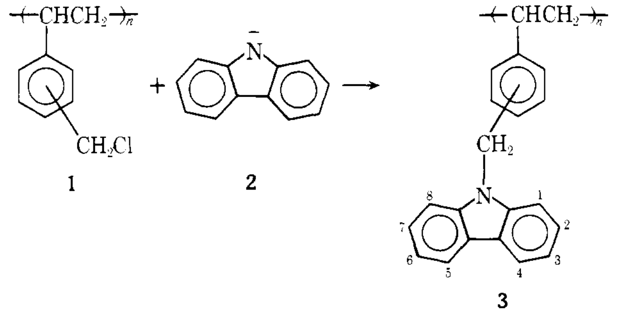
HARRY W. GIBSON* and F. C. BAILEY

Webster Research Center, Xerox Corporation, Webster, New York 14580. *Received March 29, 1976*

In recent years the chemical modification of polymers has received increasing attention,[1-4] much of it based on Merrifield's use of insoluble resins for synthesis.[5] The ability to continuously vary physicochemical properties of macromolecules by chemical modification has prompted us to examine several such types of reactions on soluble polymers.[6-13] In previous publications we have discussed reactions of poly(vinylbenzyl chloride) (**1**) with oxygen anions (phenolates) to give polymeric ethers[7] and with Reissert compound carbanions, leading to heterocyclic polymers.[8,9,11-13] In this context the reaction of **1** with nitrogen anions was of interest.

Discussion

(A) Reaction of Potassium Carbazole and Poly(vinylbenzyl chloride). The potassium salt (**2**) of carbazole was prepared by azeotropic removal of water from an equimolar solution of potassium hydroxide and carbazole in xylene.[14] The solvent xylene was removed and replaced by dimethylformamide (DMF) and a solution of poly(vinylbenzyl chloride)[11] (**1**) in DMF was added. After stirring 2.5 h, the reaction solution was added dropwise to methanol to yield 97% of the desired poly[(N-carbazyl)methylstyrene] (**3**). Three precipitations from tetrahydrofuran (THF) into ethanol gave a nearly colorless solid, T_g = 152 °C. Anal. Calcd for $C_{15}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.18; H, 5.96; N, 4.84. Gel permeation chromatography (GPC) shows no evidence of any cross-linking or degradation processes in the reaction.



The ultraviolet spectrum of **3** is essentially identical with that of N-ethylcarbazole (Figure 1). The infrared spectrum of polymer **3** is quite similar to that of poly(N-vinylcarbazole) (Figure 2).

The nuclear magnetic resonance (NMR) spectrum possesses a high field signal (δ 0.5–2) due to the protons of the backbone $CHCH_2$ groupings and a signal at δ ~4.8 due to the