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Nonlinear Changes in Specific Volume. A Route To Resolve an Entropy Crisis

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The existence of a reentrant phase diagram, possessing a high-temperature and high-pressure maximum, has recently been reported for the polymer poly(4-methyl-1-pentene).[1−4] This reentrant phase behavior recalls the general phase diagram proposed by Tammann.[5] Within this phase diagram a region, referred to as the reentrant region, exists where the entropy of a crystal is greater than that of its liquid. The existence of a crystal having entropy greater than its liquid is in contradiction to the Kauzmann paradox.[6] We show how a reentrant phase diagram can exist without invoking a paradox.

Poly(4-methyl-1-pentene), P4M1P, is a semicrystalline polymer having an unusual specific volume relationship, where the specific volume of the crystal is greater than that of the amorphous below 50 °C.[1] The crystalline phase of P4M1P normally contains helical chains with seven monomer units per two helical turns. These helices are packed in a tetragonal lattice; the unit cell parameters are $a = b = 18.66$ Å and $c = 13.80$ Å.

The semicrystalline nature of polymers arises due to kinetic restrictions during crystallization. The coexistence of the crystalline and amorphous phase allows direct measurement of the difference in specific volume. Using small-angle X-ray scattering (SAXS) techniques, the difference in specific volume can be determined.[7] Simultaneous data collection of wide-angle X-ray scattering (WAXS) provides information regarding possible phase transitions. Synchrotron radiation provides the possibility to perform simultaneous time-resolved SAXS/WAXS studies combined with high-pressure equipment.[3] The used experimental technique allows the determination of the specific volume difference as a function of both pressure and temperature. The evolution of the difference in specific volume is determined in both isothermal and isobaric experiments in the pressure−temperature phase diagram.

Figure 1 shows SAXS data recorded in-situ during isothermal and isobaric experiments. Figure 1a shows the variation in intensity on cooling at a fixed pressure of 32 MPa. From this figure it is evident that the intensity decreases sharply during the initial stages of cooling, followed by a more gradual decrease toward a minimum. Upon further decrease of temperature an increase of intensity is observed. The observed minimum corresponds to a $\Delta V = 0$ point. From the variation in intensity, the variation in specific volume difference is obtained. A schematic representation is shown in the inlay; the continuous part refers to the experimental data, and the dashed part refers to the series of experiments along similar paths. Figure 1b shows the variation of intensity with increasing pressure at 100 °C. From this figure it is evident that initially the intensity decreases to zero, followed by an increase toward a maximum. On increasing pressure further a second decrease in intensity is observed. The inlay shows a schematic representation of the variation of specific volume difference, as observed in Figure 1b. From here it is concluded that the influence of increasing pressure or decreasing temperature results in the same variation of specific volume difference. From the combined set of experiments under isobaric or isothermal conditions, four distinct features related to the specific volume difference relevant in the pressure−temperature phase diagram are assigned. The distinct features are a sharp change of the slope of the ΔV line

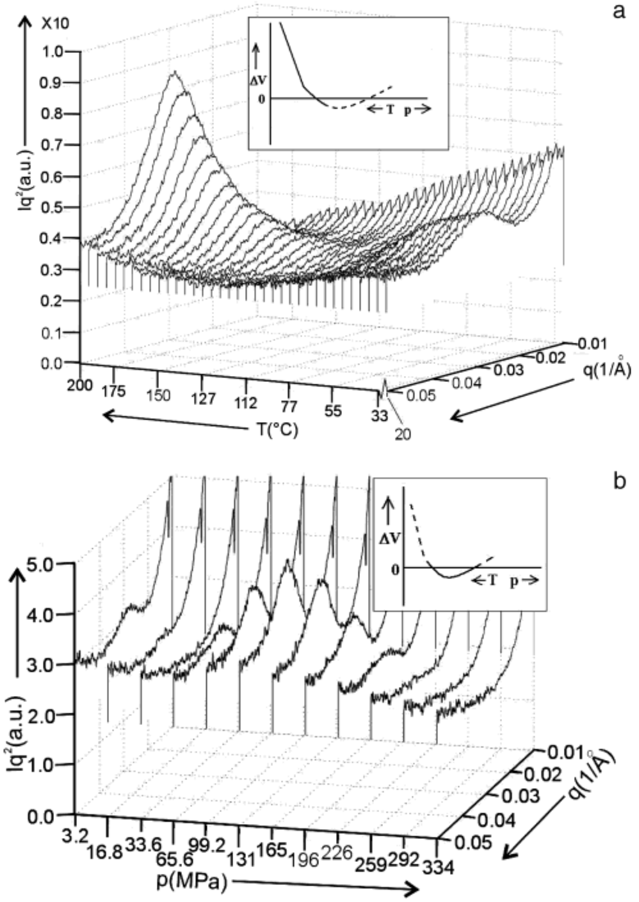

Figure 1. Evolution of SAXS patterns during (a) an isobaric experiment at 32 MPa and (b) an isothermal experiment at 100 °C. As mentioned, the scattered intensity is proportional to the difference in specific volume between the crystalline and amorphous phase in the semicrystalline polymer. The variation in specific volume difference in isobaric and isothermal conditions, with decreasing temperature and increasing pressure, respectively, is shown in the inlay of the figures. The solid part of the line corresponds to the data presented in the figure; the dashed part of the line refers to data obtained from another set of experiments. From these figures two $\Delta V = 0$ points, one in the lower pressure region and the other in the higher pressure region, can be determined, along with a ΔV maximum positioned between the two $\Delta V = 0$ points. The scattering vector q refers to the scattering angle. The z-axis refers to the Lorentz corrected intensity.

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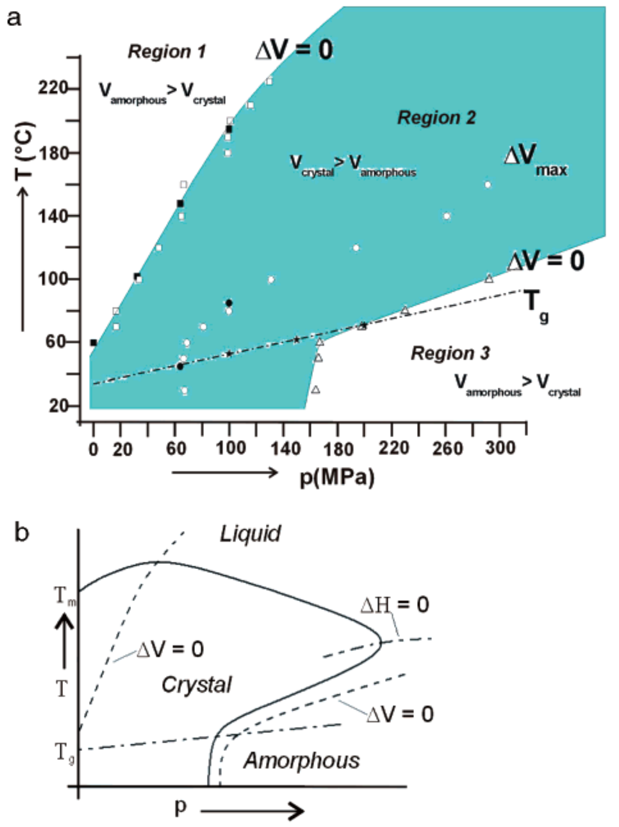

Figure 2. From a series of experiments similar to those shown in Figure 1, (a) summarizes the obtained $\Delta V = 0$ and ΔV maximum points in a $p-T$ diagram. Open symbols refer to isothermal measurements, closed symbols to isobaric measurements, and the stars are measured glass transition temperatures. The two resultant $\Delta V = 0$ lines divide the $p-T$ diagram into three regions: regions 1 and 3 correspond to the normal specific volume difference relationship where $V_{\mathrm{amorphous}}$ is greater than V_{crystal}, and the shaded region 2 corresponds to the unusual specific volume difference relationship where V_{crystal} is greater than $V_{\mathrm{amorphous}}$. Within region 2, which is bounded by the two $\Delta V = 0$ lines, the ΔV_{max} line is located. The T_g line, obtained from PVT measurements, is shown in this figure. The influence of the glass transition on the trajectory of the second $\Delta V = 0$ line and the ΔV_{max} line is evident. A schematic $p-T$ phase diagram is presented in (b); the two obtained $\Delta V = 0$ lines, shown as the dashed lines, govern the trajectory of the phase transition line, shown as a continuous line, in both the normal and reentrant region of the phase diagram. At the reentrant point the phase transition line intersects with the anticipated $\Delta H = 0$ line, shown as a dash–dot line.

as a function of pressure or temperature, a $\Delta V = 0$ point, a maximum in ΔV, and a second minimum in ΔV.

The understanding of the origin of the observed second ΔV minimum requires consideration of the anticipated phase transition (from crystalline tetragonal to amorphous) at low temperature and elevated pressure.[1] The simultaneously recorded WAXS data confirm the anticipated phase transition. From simultaneous SAXS/WAXS studies it is evident that as the SAXS intensity approaches zero, the phase transition takes place. Moreover, the observed ΔV maximum is located at much lower pressure than the phase transition. The absence in the difference of electron density fluctuations in the amorphous phase explains why no return of SAXS intensity is observed after the second ΔV minimum. From this it is concluded that the second ΔV minimum is a second $\Delta V = 0$ point.

Figure 2a summarizes the distinct features, the two $\Delta V = 0$ points and the ΔV maximum, for the complete set of isobaric and isothermal experiments similar to the experiments described in Figure 1. The figure also includes a glass transition line (T_g) based on pressure–volume–temperature measurements. The obtained line is in accordance with the earlier reported data.[3] The influence of the glass transition on the slope of the ΔV maximum line and the second $\Delta V = 0$ line is evident from the figure. An explanation for this change in slope is provided by the decrease of the difference between the expansion coefficients of the crystal and the amorphous below the glass transition temperature. When changes in the specific volume difference are combined with phase transition data obtained from simultaneous WAXS studies and previous work,[3] the schematic phase diagram, shown in Figure 2b, is obtained. Considering the differences in specific volume, the phase diagram is divided into three regions: Region 1, positioned left of the first $\Delta V = 0$ line in the phase diagram, shows a positive $\mathrm{d}T_m/\mathrm{d}p$ slope, corresponding to a greater specific volume of the liquid than the crystal, in accordance with the Clapeyron equation. Region 2, positioned between the two $\Delta V = 0$ lines, shows a negative $\mathrm{d}T_m/\mathrm{d}p$ slope, corresponding to a greater specific volume of the crystal than the liquid. The slope $\mathrm{d}T_m/\mathrm{d}p$ changes to positive after the inversion of the enthalpy difference. Considering the Clapeyron equation, the specific volume of the crystal will remain greater than that of the liquid. Region 3 is positioned below the second $\Delta V = 0$ line. The phase transition line cannot intersect with the second $\Delta V = 0$ line and enter region 3 because of the positive slope of the second $\Delta V = 0$ line. If the intersection were to take place, $\mathrm{d}T_m/\mathrm{d}p$ would have to be zero according to the Clapeyron equation. Thus, the second $\Delta V = 0$ line governs the trajectory of the phase transition line in the reentrant region of the phase diagram.

From Figure 2b the reentrant behavior of the crystalline phase is evident. The reentrant point in the phase diagram is defined as the point where $\mathrm{d}T_m/\mathrm{d}p$ is infinite. At this point, considering the Clapeyron equation, both ΔH and ΔS are equal to zero. Below this point in the $p-T$ diagram, in the reentrant region, ΔH and ΔS are negative at the phase transition line. The Kauzmann paradox defines a transition temperature (T_K) to be the temperature at which ΔS is equal to zero.[8,13] The experimental observations are that in this polymer T_K is higher than the experimentally observed T_g in the reentrant region of the phase diagram. A possible explanation for the unusual observation, where the entropy of the crystal is greater than that of the liquid, is provided on consideration of the vibrational entropy contribution (S_{vib}).[9,10]

In earlier work, Gibbs and DiMarzio[11] considered the difference in vibrational entropy between the liquid and crystal to be negligible. Since the configurational entropy of the ideal crystal is zero, the entropy difference between the liquid and crystal was taken to be solely the configurational entropy (S_{conf}) of the liquid. Recent work,[12] taking water as an example, has shown that the vibrational entropy contribution is dependent upon the specific volume. This means that a significant difference in vibrational entropy between liquid and crystal can occur when a difference in specific volume is present. In region 2 of the phase diagram shown in Figure 2a the specific volume of the crystal is greater that that of the liquid, which means that the vibrational entropy contribution in the crystal will be greater that that in the liquid. On decreasing temperature and entering the

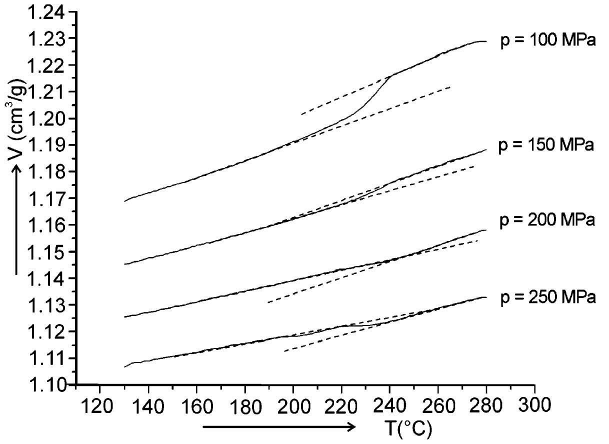

Figure 3. Specific volume as a function of temperature at different pressures is determined by PVT measurements. On cooling the material crystallizes around 230 °C, at low pressures the commonly observed contraction upon crystallization occurs, and at high pressures the opposite is observed; the material expands upon crystallization. The dashed lines are extrapolations of the specific volume of the liquid and of the semicrystalline solid. Where these lines intersect, a $\Delta V = 0$ point is situated; it is observed that at 200 MPa the crystallization occurs at the $\Delta V = 0$ line.

reentrant region of the phase diagram, the configurational entropy contribution of the liquid will decrease, and the situation will occur where the vibrational entropy of the crystal will exceed the sum of the vibrational and configurational entropy of the liquid. Thus, the origin of the apparent entropy crisis in the reentrant region is the unusual specific volume difference between the crystal and the liquid. The apparent entropy crisis[13] is resolved when the difference in specific volume between the liquid and the crystal returns to normal, as occurs in region 3 of the phase diagram shown in Figure 2a. These experimental findings show that the Kauzmann paradox, and therefore the entropy viewpoint of the glass transition,[8] does not apply to this polymer. The linear extrapolation of the entropy of the liquid to absolute zero temperature, in which the Kauzmann paradox is based,[6] is shown to be nongeneral. The nonlinearity of the entropy of the liquid at low temperature is caused by the nonlinear variation of the specific volume difference between the liquid and crystal (shown in the inlay of Figure 1a,b) with pressure or temperature. Since the WAXS results show no nonlinearity for the specific volume of the crystal, the nonlinearity in specific volume difference is attributed to the nonlinearity of the specific volume of the liquid.

In region 2 of the phase diagram (Figure 2a), where the specific volume of the crystal is greater than that of the liquid, the possibility arises that on crystallization expansion will occur, in contrary to the normally observed contraction on crystallization. Figure 3 shows the pressure–volume–temperature (PVT) results for P4M1P; the specific volume as a function of temperature is shown at different pressures. From the figure it is obvious that at pressures corresponding to region 1 of the phase diagram contraction occurs upon crystallization. At higher pressures, when the crystallization occurs in region 2, the expansion upon crystallization, similar to ice/water, is observed. The shape of the first $\Delta V = 0$ line implies that when crystallization occurs at lower temperatures, region 2 of the phase diagram will be entered at lower pressures. It is possible to vary the crystallization temperature by altering the molar mass or introducing defects (stereodefects, comonomers) into the polymer. Figure 4 shows the expansion on crystallization at 250 MPa for two different grades of P4M1P having different crystallization temperatures. From Figure 4a,b it is concluded that by lowering the crystallization temperature the amount of expansion increases, whereas the $\Delta V = 0$ point at this pressure (250 MPa) remains at the same temperature. It is to be noted that while the slope of the specific volume of the liquid with varying temperature is the same for both grades, the slope of the specific volume of the semicrystalline polymer is dependent upon the crystalline fraction present in the material.

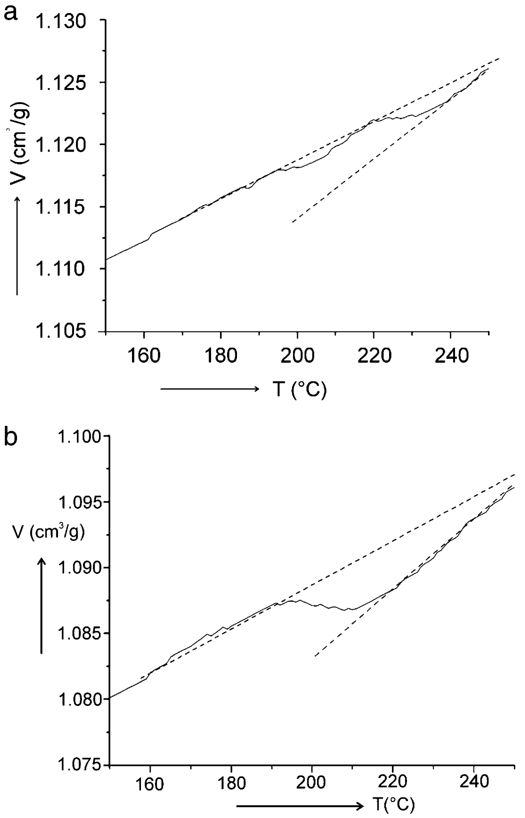

Figure 4. Specific volume as a function of temperature at 250 MPa for (a) the same material as in Figure 3 and (b) a lower molecular weight material with a lower melting point. It can be seen that, independent of grade, the $\Delta V = 0$ point remains at the same position, so that by lowering the crystallization temperature, the amount of expansion is increased and the pressure at which expansion starts occurring is decreased in accordance with the $\Delta V = 0$ line of Figure 2. The divergence of the two dashed lines in (b) is greater than in (a) due to the higher crystallinity of the low molecular weight sample.

Preliminary studies performed on a series of other polymers, such as syndiotactic polystyrene,[14] syndiotactic poly(*p*-methylstyrene),[15] and poly(diethylsiloxane), show unusual features in their phase diagrams similar to those observed in P4M1P. These preliminary results suggest that by controlling the molecular architecture of the polymer with respect to the side group nonlinearity in the specific volume behavior of the liquid can be generated, which, in combination with a high specific volume of the crystal, allows the existence of reentrant behavior. This nonlinear behavior of the liquid is not restricted to the specific volume; preliminary results show a large deviation of the viscosity dependency on temperature of P4M1P from normal liquids, perhaps similar to concepts proposed on fragile liquids.[16,17]

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