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Pressure induced order–disorder transition in a diblock copolymer

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Abstract

Polymers are known to undergo order↔order and order↔disorder transitions, when subjected to a change of pressure, temperature, solvent, pH of the medium etc. The molecular processes, which alter the volume of the system, are found to be highly sensitive to the pressure. In the present communication Zimm and Bragg model of helix↔coil transition has been modified to interpret the experimental data of pressure induced phase transition in polystyrene–polybutadiene [PS–PB] at different pressurization rates, as reported by Migler and Han, utilizing the Birefringence and small angle neutron scattering technique. An expression for the degree of order is obtained from the grand partition function for the entire chain in terms of nucleation parameter, which controls the transition width. The nucleation parameter σ increases with the increase in the ODT temperatures of the system. The phenomenon of hysteresis has been discussed in relation to the pressurization rate, which increases/decreases with the corresponding increase/decrease in the pressurization rate. The theoretical transition curves are found to be in good agreement with experimental data.

Keywords: Phase transition; Pressure; Copolymer

1. Introduction

Molecular processes which alter the volume of the system are found to be highly sensitive to the pressure. Pressure in addition to temperature has been one of the most important thermodynamic parameter for characterizing the behaviour of the bio/macromolecular-systems [1–9]. Because of the availability of wide ranges of pressurization rates, the kinetics of these systems can be investigated by the application of pressure as an experimental probe. Kalman B. Migler and Charles C. Han have reported, an experimental study on the pressure induced order–disorder transition (ODT) in perdeuterated polystyrene–polybutadiene [PS–PB], a diblock copolymer, synthesized in the laboratory of J. Mays and solvated in dioctyl phthalate, to lower the ODT [10].

As a part of our ongoing research work on vibrational analysis, phonon dispersion [11–17] and phase transition [18–22] in a variety of macromolecules, here in the present communication Zimm and Bragg model of helix↔coil (order↔disorder) transition has been modified to explain the phenomenon of pressure induced phase transition in the diblock copolymer [PS–PB]. The diblock copolymers represent a model system for the study of several technologically important areas such as compatibilization, self-assembly and micro-phase transition. In one of our recent publications [18], the same Zimm and Bragg model was modified, to explain the phenomenon of the temperature induced phase transition in poly(β-benzyl-L-aspartate) [PBLAsp] and it is copolymer copoly((β-stearyl-L-aspartate-β-benzyl-L-aspartate) [copoly(SLAsp-BLAsp)].

2. Theory

The present theoretical approach is a modification of the Zimm and Bragg model [9] enunciated for helix↔coil (order↔disorder) transition and has earlier been used to explain an order↔order transition in the case of PBLAsp and it copolymer [copoly(SLAsp-BLAsp)] as well as in poly-L-proline [18,21] and order↔disorder transition in the case of polyethylene [20]. An expression for degree of order 'Q' is obtained from the grand partition function for entire chain in terms of nucleation parameter. Taking into account the nearest-neighbour interactions, the basic transition matrix 'M' is given below:

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$$M = \begin{array}{cccc} & r & k & h \\ r & \sqrt{f_r}\sqrt{f_r} & \sqrt{f_r}\sqrt{f_k} & 0 \\ k & \sqrt{f_k}\sqrt{f_r} & 0 & \sqrt{f_k}\sqrt{f_h} \\ h & \sqrt{f_h}\sqrt{f_r} & 0 & \sqrt{f_h}\sqrt{f_h} \end{array}$$

here r, k and h are segments in disordered, boundary and ordered regions of the macromolecular chain whereas f_r, f_k and f_h denote the segment partition functions of the disordered, boundary and ordered states of the macromolecule, respectively.The eigenroots of M, determined by the secular equation

$$|M-\lambda I| = 0 \tag{1}$$

are as follows:

$$\lambda_1 = \frac{1}{2}[(f_r+f_h)+\sqrt{\{(f_r-f_h)^2+4f_rf_k\}}] \tag{2}$$

$$\lambda_2 = \frac{1}{2}[(f_r+f_h)-\sqrt{\{(f_r-f_h)^2+4f_rf_k\}}]$$

$$\lambda_3 = 0$$

where I is a 3×3 unity matrix.

The partition function 'Z' for a chain of N segments is

$$Z = C_1\lambda_1^N + C_2\lambda_2^N = Z_1 + Z_2 \tag{3}$$

The fraction of disordered 'r' segments $\langle n_r \rangle = (n_r)/N$

$$<n_r> = \frac{1}{N}\left[\frac{\partial \ln Z}{\partial \ln f_r}\right] = \frac{f_r}{NZ}\left[\frac{\partial Z}{\partial f_r}\right] \tag{4}$$

For an infinite chain the fraction of disordered segments is calculated by the following equation:

$$<n_r> = \frac{\lambda_1 - f_h}{\lambda_1 - \lambda_2}$$

The fraction of segments in the ordered phase denoted by 'Q' is given by

$$Q = 1 - <n_r> = \frac{1}{2}\left[\frac{1+(s-1)}{\sqrt{\{(s-1)^2+4\sigma s\}}}\right] \tag{5}$$

where $s = f_h/f_r$ and $\sigma = f_k/f_h$ are the growth and nucleation parameters, respectively.

The following well known thermodynamic relations provide the pressure and temperature dependence of the equilibrium constant s.

$$\frac{\partial \ln s}{\partial P} = \frac{\Delta V}{RT} \tag{6}$$

$$\frac{\partial \ln s}{\partial T} = -\frac{\Delta H}{RT^2} \tag{7}$$

where $\Delta V = V_r - V_h$ and $\Delta H = H_r - H_h$ are respectively the molar volume and molar enthalpy change across the transition point. By successive integration it can be shown that s is given by the following expression:

$$s = \exp\left[\frac{\Delta V(P-P_{\mathrm{F}})}{RT}\right] \tag{8}$$

The change in molar volume for the first order transition is calculated by using the Clausius Claypeyron's equation, i.e.

$$\frac{\mathrm{d}T_{\mathrm{F}}}{\mathrm{d}P} = \frac{T_{\mathrm{F}}(V_{\mathrm{r}} - V_{\mathrm{h}})}{\Delta H} \tag{9}$$

where P_{F} and T_{F} are the transition pressure and the fixed value of temperature at which the pressure transition takes place.

3. Results and discussion

We report here an extension of the Zimm and Bragg model [9] to explain the pressure induced order↔disorder transition in [PS–PB]. Theoretical transition curves for a polymer chain of length N have been obtained from Eqs. (5)–(9). However, for the calculation of crystallinity (degree of order), Eq. (5) is the final equation. These curves are found to be linear in the transition region. The linear part when extrapolated can give the value of the pressure known as the melting pressure P_{Tm} at which the last crystallite disappears. The melting pressure depends on the sharpness of the transition curve. In general the sharpness of the transition depends upon the value of enthalpy change, and the fluctuations around the transition point. The holistic effect of these is reflected in the magnitude of 'σ' and the half width of transition profile. The smaller the value of σ, sharper is the transition.

In contrast to the significant variation in values of growth parameter 's' with pressure, the nucleation parameter 'σ' has a weak dependence on pressure. Therefore, for all theoretical purposes the values of nucleation parameter at the fixed ODT temperatures are assumed to be constant and independent of pressure as well as other surrounding interactions. The entropy changes associated with the transitions at various temperatures fluctuate within a very narrow range, an average value of 2.3 Cal/mole-K is assigned to it for all pressures.

Birefringence study by Migler and Han on the diblock copolymer [PS–PB], to measure pressure induced order↔disorder transition at fixed ODT temperatures shows that, with the increase in temperature, the amount of pressure needed to bring the ordering increases. They have plotted the Intensity (Birefringence) as well as the small angle neutron scattering (SANS) data versus pressure for a range of ODT temperatures at the different pressurizing rates. In the present communication, the birefringence data as reported by Migler et al. has been used as an excellent parameter to follow the pressure induced order↔disorder transition [1], simply due to the

Table 1
Transition parameters for pressure induced phase transition in [PS–PB] at pressurization rate = 6.9×10^{-3} MPa/s

S.no.	ODT temperatures in Kelvin	Transition pressure in MPa	Nucleation parameters
1.	353	24.8	4.0×10^{-4}
2.	359	54.4	6.0×10^{-4}
3.	365	87.2	8.0×10^{-4}

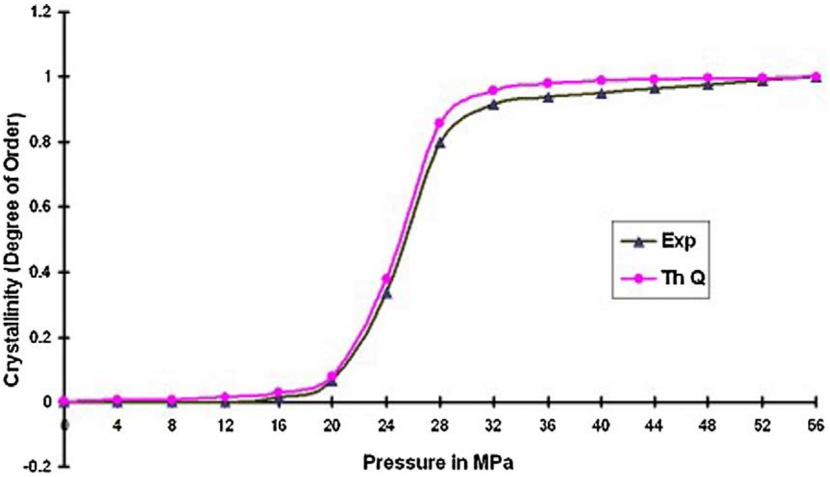

Fig. 1. Schematic representation of crystallinity as a function of pressure in [PS–PB] at ODT temperature (353 K) with pressurization rate 6.9×10^{-3} MPa/s.

greater precision and sensitivity of birefringence technique over the neutron scattering, The transition parameters for pressure induced transition in [PS–PB] are given in Table 1. In the case of polymers such as polyglycine, polyproline, polyethylene the σ values are generally of the order of 10^{-3}–10^{-4} [23]. The σ values in case of [PS–PB] are also theoretically found in this range. The experimental points (represented by ▲) and theoretical points (represented by ●) corresponding to the various degrees of crystallinity have been plotted in Figs. 1–3 (crystallinity versus pressure curves). These curves represent the pressure induced order↔disorder phase transition in [PS–PB] at the fixed ODT temperature ranging from 80 to 92 °C. Comparison of the σ values, arrived at theoretically (refer to Table 1) shows that the values of nucleation parameter σ increases with the increase in the ODT temperatures of the system. The variation of σ is also found to be almost linear with temperature. The larger the value of σ, smaller will be the free energy change in creating the transition/boundary interface [24]. This is also reflected in the sharpness of the transition profiles as observed by Migler et al. supporting the aforesaid theoretical observations. Since the rise in temperature not only leads to the increase in the value of nucleation parameter, which reflects the greater ease of nucleation at higher temperature, but also leads to the increase in the entropy of the system, resulting in a higher degree of disorder in the system. This requires further more pressure to bring the chains to their van der Waal's radii in order to have the ordered system. Hence the order of the theoretical values of σ, i.e. $\sigma(\mathrm{ODT}_{92})>\sigma(\mathrm{ODT}_{86})>\sigma(\mathrm{ODT}_{80})$ is consistent with the experimentally observed comparative degree of disorder in [PS–PB]. The degree of disorder is also manifested by the shift in transition pressure as observed experimentally, i.e. $P_{\mathrm{T}92}>P_{\mathrm{T}86}>P_{\mathrm{T}80}$. The increase in the transition pressure with the increase in transition temperature is experimentally reported to be almost linear, this suggests that the pressure induced order↔disorder transition in [PS–PB] is analogous to the melting of paraffins and polyethylene.

The importance of pressurization rate in the pressure induced ordering process has also been theoretically studied in terms of nucleation parameter σ for ODT at 359 K. The experimental data for the ordering process corresponding to the two different pressurization rates, i.e. 6.9×10^{-4} MPa/s

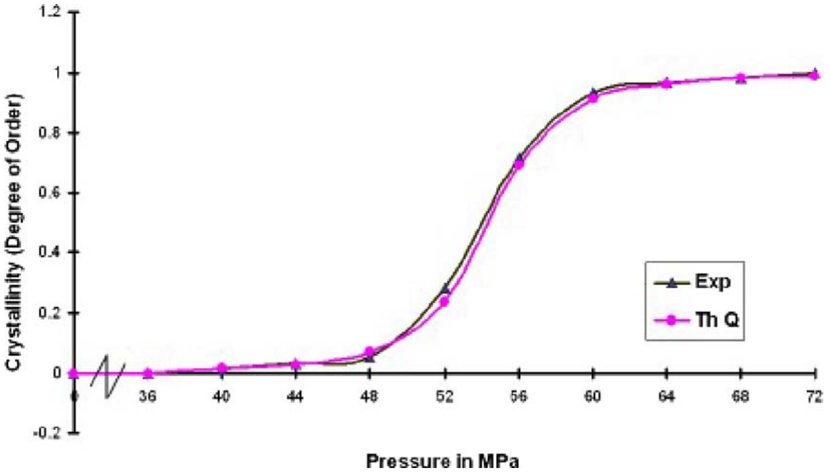

Fig. 2. Schematic representation of crystallinity as a function of pressure in [PS–PB] at ODT temperature (359 K) with pressurization rate 6.9×10^{-3} MPa/s.

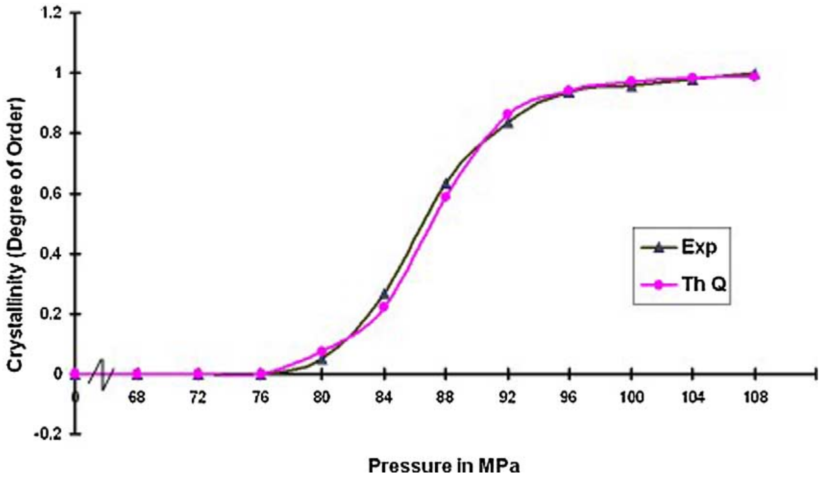

Fig. 3. Schematic representation of crystallinity as a function of pressure in [PS–PB] at ODT temperature (365 K) with pressurization rate 6.9×10^{-3} MPa/s.

and 6.9×10^{-3} MPa/s, have been used to obtain the theoretical ODT curves. The theoretical curves (refer to Fig. 4) drawn for two different σ values correspond to the two pressurization rates. These curves fit well with the experimental curves. They represent the ordering behaviour of [PS–PB] at the different pressurization rates. In the ordering process, the nucleation of grains of proper (critical) size is of utmost importance, which is followed by the growth of the grains. This fact makes the ordering process clearly a collective/cooperative phenomenon. The slower the pressurization rate, the better is the opportunity for nucleation to take place. This leads to the higher degree of sharpness of phase transition. Hence the ordering process as such depends on the pressurization rate, whereas the disordering process is completely independent of pressurization rate because it requires only the rearrangement/reorientation of the individual molecules.

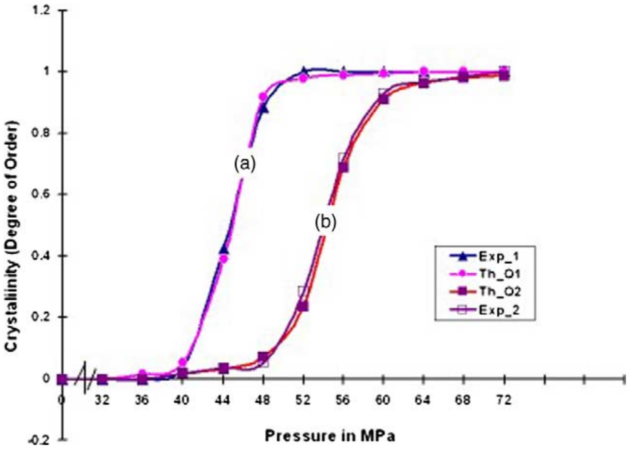

Fig. 4. Schematic representation of crystallinity as a function of pressure in [PS–PB] at ODT temperature (359 K) with different pressurization rates. Family of curves (a) corresponds to pressurization rate 6.9×10^{-4} MPa/s. Family of curves (b) corresponds to pressurization rate 6.9×10^{-3} MPa/s.

Table 2
Transition parameters for pressure induced phase transition in [PS–PB] at the fixed ODT temperature (359 K)

S.no.	Pressurization rate in MPa/s	Transition pressure in MPa	Nucleation parameter
1	6.9×10^{-3}	54.4	6.0×10^{-4}
2	6.9×10^{-4}	44.5	2.0×10^{-4}

A substantial reduction in the values of σ (refer to Table 2) and the increase in sharpness of transition profile, as the pressurization rate falls sharply (10 times), have been theoretically observed (refer to Fig. 4). These facts are in full conformity with the experimental observations that the ordering curve gets shifted to the lower pressures and is accompanied by the increase in sharpness of ordering curve with the decrease in the pressurization rate. The reduction in hysteresis in [PS–PB] could be probably due to the asymmetric behaviour of the ordering and disordering processes, i.e. the ordering curve getting shifted to lower pressures while the disordering curve remaining unaffected with the reduction in the pressurization rate. Consequently the hysteresis is found to be a highly pressurization rate dependent phenomenon, which increases/decreases with the corresponding increase/decrease in the pressurization rate.

4. Conclusions

The present theoretical work on pressure induced phase transition in the synthetic diblock polymer polystyrene–polybutadiene [PS–PB], clearly demonstrates the ability of our modified Zimm and Bragg treatment to successfully organize and interpret the data on the equilibrium properties of helix↔coil transitions. The same model has been applied to explain the helix↔helix transition in a variety of macromolecules. One of the merits of the present approach leads to the explicit arrival of values of the nucleation parameter σ, which are consistent with the stabilization/destabilization of the ordered/disordered states, subjected to various kinds of environmental conditions.

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