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

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}