

Effect of pressure on the melting, crystallization and morphology of poly(alkylene succinate)s.

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[Introduction] Information on changes in thermal properties under high pressure is important for practical applications in polymer engineering because polymers are frequently subjected to pressure during processing. After it was discovered that polyethylene could form extended chain lamella under high pressure many researches have been carried out. However, not many studies have been reported on systematic homologous series of polymers to understand their melting behavior when exposed to high pressure. In this study the melting temperature of a homologous series of linear polyesters of the succinate group under high pressure was investigated to obtain the pressure dependence of melting (dT/dp) and is discussed in relation to the chemical structure.

[Results and Discussion] The thermal transitions of poly(ethylene succinate) [PES], Poly(tetramethylene succinate) [PTMS] and poly(hexamethylene succinate) [PHMS] (Fig 1) were investigated by high pressure differential thermal analysis up to 500MPa. The melting (T_m) and crystallization (T_c) temperatures were found to increase with increasing pressure and fitted the quadratic equation while the (dT/dp) decreased. Phase diagrams (Fig 2) were newly determined for these polyesters and the thermodynamic variables, enthalpy and entropy of fusion were obtained from the Clausius-Clapeyron equation. Melting peak profiles remained unchanged under high pressure and at atmospheric pressure after high pressure crystallization suggesting no crystal transition and lamella thickening as seen in polyethylene [1]. In homologous aromatic polyesters, the melting temperature was found to increase with pressure and the pressure dependence of melting, dT/dp , was found to decrease with increasing ethylenic group in the structure and was attributed to the change in entropy due to conformational disordering because of increased flexibility [2]. The $dT/dp_{(p=0)}$ in linear polyesters did not show a decreasing relationship with increasing number of $-\text{CH}_2-$ groups in the structure and therefore, the same explanation as in aromatic polyesters does not hold true for linear polyesters. The $dT/dp_{(p=0)}$ of the polyesters was related to the change in entropy of fusion at melting and change in specific volume as shown in table 1. Total entropy of fusion of a crystal can be split into orientational and conformational disordering. In rigid molecules, contributions from orientational can be negligible and is mainly due to conformational changes. However, in linear polyesters, the dT/dp may be affected by entropy from both contributions due to the absence of the rigid group.

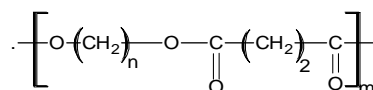


Fig. 1 Chemical structure of poly(alkylene succinate).

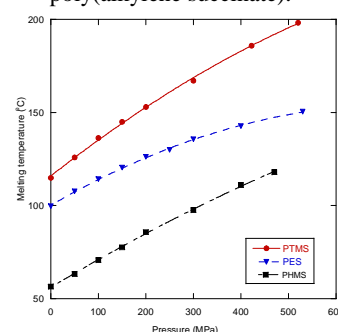


Fig. 2 Pressure dependence of melting temperatures.

Table 1. Parameters obtained from high pressure measurement

alkylene	n	M_w	M_w/M_n	T_m ($^{\circ}\text{C}$)	dT/dp ($^{\circ}\text{C}/\text{MPa}$)	Δv (cm^3/g)	ΔS ($\text{J}/\text{K}\cdot\text{g}$)	ΔH (J/g)	θ (degree of crystallinity)
Ethylene	2	33134	1.86	99	0.146	0.0398	0.270	100	56
Tetramethylene	4	72000	1.63	113	0.201	0.0275	0.137	52.6	26
Hexamethylene	6	28500	1.90	56	0.165	0.0267	0.159	53.2	52

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