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MESOPHASE TRANSITION OF POLYDIETHYLSILOXANE

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Abstract Constant pressure DSC of Polydiethylsiloxane (PDES) shows a rigid crystal to condis crystal disordering (T_d) at 206 K, and a melting transition (T_i) at 276 K. In addition PDES shows a glass transition T_g around 135 K and a small endotherm associated with loss of residual order around 295-300 K. PDES can be annealed just below T_i increasing Xc from typically 0.5 to 0.72.

INTRODUCTION

PDES was first reported to exhibit multiple phase transitions by Lee and coworkers. [1,2] Beatty [3,4,5] reported the T_g around 130 K and described the 200 K transition as a "solid-solid" transition which sometimes appeared as a double peak depending on the prior cooling rate of the sample. Beatty [4] and later, Godovsky [6,7,8] attributed this phenomenon to crystal dimorphism. Beatty reported a melting transition (T_m) around 270 K to a "liquid crystalline phase" which showed a small transition at 297 K. Pochan [6,9,10] reported dielectric and nuclear magnetic relaxation studies suggesting onset of motion in the solid just below 200 K and translational motion starting around 258-278 K. X-ray scattering [6] showed the persistence of residual order above T_i at least 300 K.

Experimental

The sample of PDES was provided by Dr. Boyer and is the same used by Karasz and Beatty [4]. DSC measurements were made using a modified Mettler TA-2000B. Low temperature X-ray scattering work was performed on a Simon/de-Wolff heating X-ray unit.

Results

Typical DSC traces of PDES cooled under different conditions are shown in Fig. 1. PDES quenched (Q) at 343 K in liquid nitrogen shows a glass transition (T_g) at 135 K, a cold organization exotherm at 165 K and a transition to the isotropic state (T_i) at 270 K. PDES quenched (pQ) near the organization temperature (T_o) shows T_g, the cold organization exotherm, a disordering transition (T_d) to the mesophase at 197 K and a doubling of the 270 K transition (T_i) PDES cooled at 10 K/min (C) show the characteristic T_g, T_d and T_i transitions. PDES annealed at 264.5 (A) shows a rise in T_d to 206 K and T_i to 276 with an improvement of X_c = 0.72.

A series of annealing experiments at 258, 264.5, 265, 271 K for 1 hour are shown in Figure 2. Not annealed PDES (N/A) is shown for comparison. No significant change is observed for longer annealing times. Increasing the annealing temperature toward 264.5 K gave a continuous increase in T_m. Above 264.5 K melting of the mesophase occurs with recrystallization on cooling. There is a rise in T_d corresponding to the rise in T_i. Annealing near T_d (200 K) has no effect on either T_d or T_i.

The ordering temperature (T_o) and crystalli-

zation temperature (T_c) are shown in Figure 3 for the cooling and subsequent heating of PDES at 10 K/min. Typically, a large supercooling is observed for T_o (30-40 K) while the supercooling for T_c is small (2-5 K).

X-ray scattering patterns in the range 103-292 K are given in Figure 4. At 258-263 K (above T_d but below T_i) a loss of short range order and a doubling of the main peak at 4.8° are seen, suggesting conformational change. At 288-293 K persistence at 4.8° (1.0 nm) is seen. Close examination of the X-ray films shows persistence to 330 K. Optical microscopy carried out in this range shows a loss of birefringence above 276 K.

Experimental values of ΔH_d and ΔH_i plotted versus ΔC_p for different X_c are given in Figures 5 and 6. The limiting values for amorphous and 100% crystalline PDES are given in Table I with values reported by Beatty [4,5] and Godovsky [6].

Discussion

PDES clearly shows two first order transitions: T_d (206 K) and T_i (276 K). At T_d X-ray scattering shows small changes in order. Results of dielectric studies [5] indicate a large change in E' near T_d and nuclear magnetic relation studies [9] show a 3-fold jump in T_{2e} around 194 K for the crystalline phase suggesting onset of motion. However, ΔS_d = 8.5 J/(k-mol) is too large for a crystal-crystal transition. We believe T_d is a rigid crystal to condis mesophase transition.

Above T_i X-ray scattering shows substantial loss of order. An increase in τ_1 and τ_2 from

nuclear magnetic relation [9] reports "translational motion" in amorphous regions of the polymer above 258 K and in crystallites after melting above 268 K. Dielectric [6] and nuclear magnetic relaxation [9] studies suggest some order is gradually lost over the range 195-270 K with long range order lost above 276 K, explaining ΔS_i = 6.3 J/(k-mol) is smaller than expected. (ΔS_{total} is expected to be 28.5 J/(k-mol)).

Annealing and crystallization experiments also associate long range order with T_i. The continuous rise in T_i, simultaneous rise of T_d, and increased crystallinity with increasing annealing temperatures below T_i suggest important long range order is associated with T_i and also discredit possibilities of crystal dimorphism. [6,7,8] Large supercooling of T_o (below T_i) of 30-40 K and small supercooling of T_c (2-5 K) indicates order is set at T_o with a need for a nucleation process, while local order is set at T_c without nucleation. Models for the minimum energy conformation of PDES [11] suggest two low energy conformations: at 55/10 helix (E=0) and bent backbond (E = 1.7 kJ/mol). In the mesophase these two conformations may coexist and interconvert with "collapse" to the more stable helix with a small E_a at T_c.

Conclusion

Amorphous PDES shows a glass transition (T_g at 135 K with C_p = 30.65 J/(k-mol)).

Ordered PDES shows a rigid-crystal-condis mesophase transition (T_d at 206 K with ΔH_d = 1.7 kJ/ol and ΔS_d = 8.5 J/(k-mol)).

The condis-mesophase of PDES shows a transition to a highly disordered state (T_t) at 276 K with ΔH_t = 1.7 kJ/mol and ΔS_t = 6.3 J/(k-mol).

PDES may be annealed below T_t with an increase of X_c from 0.4-0.5 to 0.72 and a rise of T_d from 197 K to 206 K and a rise of T_t from 265 K to 276 K. Large supercooling (30-40 K) is observed for T_o and little supercooling is seen for T_c suggesting long range order is set at T_o.

A persistence of order above T_t is seen by X-ray scattering to 330 K, although the transition to the isotropic state is small and not easily reproduced.

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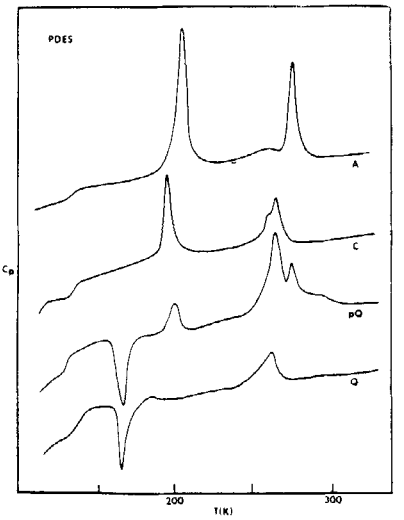

FIGURE 1: DSC of PDES

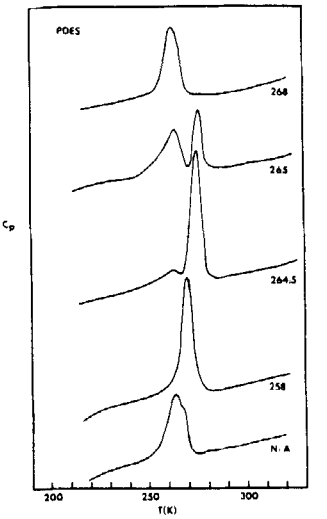

FIGURE 2: Annealing of PDES

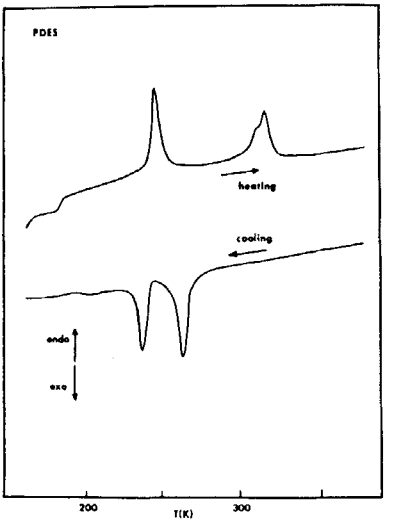

FIGURE 3: Cooling and heating DSC of PDES

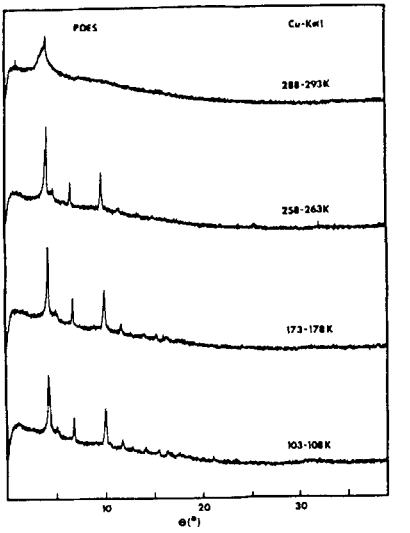

FIGURE 4: Variable Temperature X-ray Scattering of PDES

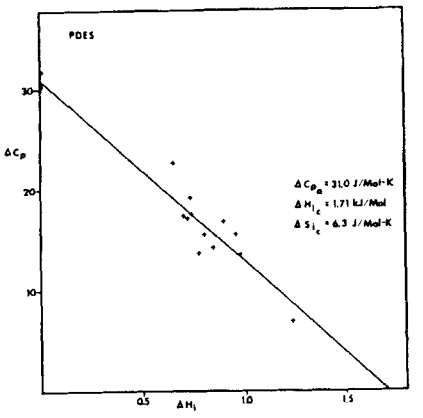

FIGURE 6: C_p vs. H_i

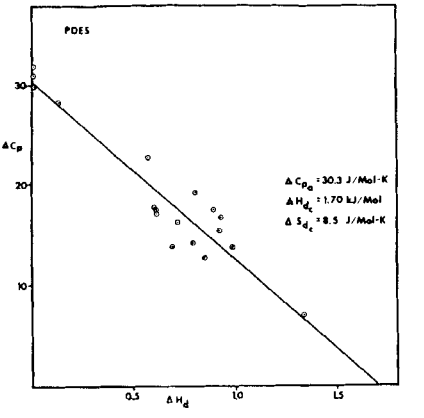

FIGURE 5: C_p vs. H_d

	Beatty[4,5]	Godovsky[8]	Wunderlich	
ΔC_p	17.5	37.0	30.65	J/(K-mol)
ΔH_d	3.40	1.73 (2.16)	1.70	kJ/mol
ΔS_d	17.	8.65 (10.8)	8.5	J/(K-mol)
ΔH_i	1.02	2.85 (2.71)	1.71	kJ/mol
ΔS_i	3.78	10.6 (10.0)	6.3	J/(K-mol)
ΔH_u	(small)	0.28	(small)	kJ/mol

TABLE 1: Thermodynamic Transitions of PDES