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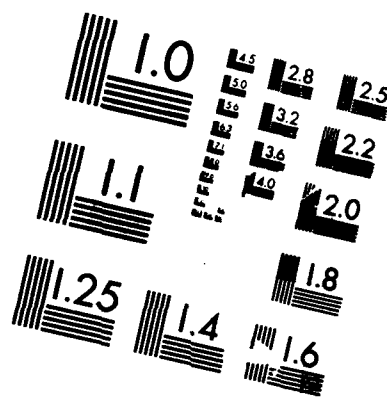
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Pressure-Induced Phases in a Thermotropic Polyester

by

B. S. Hsiao, M. T. Shaw and E. T. Samulski

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Liquid Crystalline Polymer Research Center
Institute of Materials Science, U-136
The University of Connecticut
Storrs, CT 06268

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PRESSURE-INDUCED PHASES IN A THERMOTROPIC POLYESTER

B. S. Hsiao, M. T. Shaw and E. T. Samulski

Liquid Crystal Polymer Research Center
Institute of Materials Science
The University of Connecticut
Storrs, Connecticut 06268

ABSTRACT

Studies of a copolyester of 20% hydroxybenzoic acid, 40% isophthalic acid and 40% hydroquinone, a mesomorphic polymer, were carried out under pressure. The phase behavior was characterized by the X-ray diffraction, thermal analysis and high pressure DTA techniques. It was found that pressure induced a new crystal habit in the solid and a new mesophase in this polymer. All thermal transitions have been summarized in a proposed phase diagram. The finding of pressure-induced mesomorphism confirms the possibility of extending the range of polymers which might exhibit liquid crystallinity.

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INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) are currently being intensively investigated because their ordered fluid phases are precursors to high performance polymeric solids (fibers, films and injection-molded articles). In an effort to broaden the range of materials that might exhibit liquid crystallinity, we have examined the role of pressure on polymer melts. This work was motivated by observations that low-molecular-weight liquids may be transformed into mesophases at elevated pressures.¹ The subject of this study is a copolyester, "HIQ-20",² whose composition lies just inside of the mesophase range. We find that at elevated pressure, the previously reported mesophase of HIQ-20 is stabilized as anticipated and moreover, a second mesophase is induced at high temperatures. Additionally, we observe that cooling the mesophase into the solid state under moderate pressures (≥ 300 bar) yields a morphology that differs dramatically from that found in the solid produced at ambient pressure. This new pressure-induced crystal phase exhibits intrinsically superior mechanical properties. This observation is particularly noteworthy because the pressure required for forming the new solid phase is comparable to or less than pressures employed in conventional processing techniques.

EXPERIMENTAL

Phase Characterization

Differential scanning calorimetry (DSC) traces of HIQ-20 at ambient pressures were measured by a Perkin-Elmer DSC Model 2 instrument. The high

pressure differential thermal analysis (DTA) thermograms and the pressure-volume-temperature (P-V-T) relations were obtained with a Instron capillary rheometer modified to operate at a maximum temperature of 380°C and a maximum pressure of 6000 bar (6 GPa). A detailed description of this apparatus has been given previously.³

Sample Preparation

The modified Instron capillary rheometer was used to prepare HIQ-20 specimens at various pressures. A Teflon rod, with a small cylindrical central chamber, encased the polymer sample (about 1 g) in the rheometer barrel. The temperature was raised above the clearing temperature of HIQ-20, whereupon pressure was applied to the Teflon-encased sample. The temperature was then reduced into the mesophase and held for 1 hour. The sample was subsequently cooled under pressure to room temperature at a rate of 3 °C min.

X-ray diffraction

The recovered pressure-annealed HIQ-20 specimens were ground into a fine powder and loaded into 0.5-mm glass capillaries for wide angle X-ray diffraction examination. X-ray powder diagrams were obtained with a Debye-Scherrer camera and by Ni-filtered Cu-K α radiation. The 2 θ -scans were derived from the X-ray films by an Optronics Model 9000 densitometer. All 2 θ scans were normalized by dividing by the total intensity count on the film.

RESULTS AND DISCUSSION

A rheological investigation and brief description of the synthesis of HIQ copolyesters at various HBA compositions has been recently reported by Kiss.⁴ It was stated in his paper that if HIQ contained less than 25% HBA, the mesomorphic behavior vanished. However, in this study, we confirmed by hot-stage optical microscopy and DSC that HIQ-20 (20% HBA) system exhibits a mesomorphic phase consisting of a melting transition (crystalline to mesomorphic) temperature of 324 °C and a clearing transition (mesomorphic to isotropic) temperature of 342 °C.

The X-ray 2θ-scans of HIQ-20 prepared at different pressures are shown in Figure 1. The 2θ-scans vary with the pressure, indicating that the structure in the solid derived from annealed fluid phases changes with the applied pressure during annealing. At atmospheric pressure, the normally observed crystalline phase K1 is formed and K1 is independent of the thermal history⁵. When the pressure is increased, K1 is lost in favor of a new structure, a pressure-induced crystal form designated K2. The X-ray powder diagrams for the low pressure (K1) form and the high pressure (K2) form are shown in Figure 2. The minimum pressure required to convert from K1 to K2 is approximately 300 bar; the 2θ-scan is independent of pressure between 300 bar and 2000 bar. At pressures between 1 bar and 300 bar, the X-ray data indicates a mixture of K1 and K2 crystal habits.

The DSC traces of K1 and K2 samples are shown in Figure 3. The first heating curve of the K2 sample exhibits an additional endothermic transition peak. This peak disappears on the second scan which resembles that of K1. Correspondingly, the X-ray diffraction pattern of this heated K2 sample shows a K1 pattern indicating that K2 has been converted to K1. Thus K1 and K2 appear

to be equilibrium phases, although not necessarily with each other. To separate the K1 and K2 transitions, HIQ-20 was melted under pressure with a high pressure DTA device³. Indeed, the DTA thermogram at high pressure (Figure 4B) exhibits multiple transitions, the lowest of which is probably to be associated with a K1 to K2 transition, although we have no other more direct evidence for this. The pressure-induced endothermic transition in the high temperature region in Figure 3 is attributed to a new mesophase, M2, as distinguished from the original mesophase, M1. The pressure dependence of these transitions are summarized in a proposed phase diagram of HIQ-20 shown in Figure 5. All data points are obtained from the peak temperatures on DTA thermograms under high pressure. The solid lines have been checked with the Clapeyron equation⁵ using P-V-T data; the broken lines symbolize proposed phase boundaries.

It is suspected that in HIQ copolyesters, HBA rigidifies the polymer and contributes to mesomorphism while IA/HQ sequences are less ordered and promote isotropic phases.⁴ There is evidence that these two structurally different components may drive micro-phase segregation, namely, an HBA-rich mesomorphic region and a HBA-depleted isotropic region might occur in similar copolyester systems.^{6,7} If HBA-rich domains segregate out in HIQ-20, one might expect to see an X-ray diffraction pattern characteristic of the HBA homopolymer. However, in the X-ray diffraction patterns of both the K1 and the K2 forms, there is no evidence for diffraction characteristic of the crystalline HBA homopolymer.^{8,9,10} Thus neither K1 nor K2 can be associated with micro-phase separation of a HBA-rich component and consequently it is reasonable to assume that HIQ-20 is a random copolyester. This conclusion agrees with Blackwell's findings on the HBA 2-hydroxy-6-naphthoic acid (HNA) copolyester system: a random primary

structure is proposed.^{11,12,13} Furthermore, all thermal transitions observed in HIQ-20 are reversible, eliminating the possibility of substantial transesterification during sample preparation.^{14,15}

We are not able to confirm with optical microscopy the nature of M1, i.e., nematic or smectic. Smectic would imply long range lateral interactions among chains that are confined to layers orthogonal to the chain axis. Our efforts to quench M1 at atmospheric pressure may support a more translationally ordered mesophase: specimens quenched from M1 in ice water (at $\approx 100^\circ\text{C}/\text{sec}$) always yielded a K1 crystal structure, implying that there is minimal reorganization of chains on cooling M1. This is consistent with our optical observation; M1 is a highly viscous mesophase. The shear viscosity (η) in HIQ-20 (20% HBA) at M1 temperatures is approximately 10,000 poise (extrapolated from Kiss's report.¹⁶) As for the identification of M2, high pressure analysis techniques such as microscopy and X-ray will be necessary.

All of these observations suggest that at ambient pressures there may be specific lateral interactions between relatively dilute segments in HIQ-20 chains in the mesophase M1 and on cooling, these interactions persist and drive the solid into crystal habit K1. Such specific interactions may be replaced by more general ones at elevated pressure yielding a solid with the K2 habit.

CONCLUSION

The 'HIQ-20' thermotropic polyester is a rather complicated polymorphic system. It has high transition temperatures and narrow mesophase ranges. The

most striking attribute of this polyester is its pressure-induced mesophase at high temperatures and the pressure-induced crystal phase. These findings indicate that it may be possible to broaden readily the range of mesogenic polymers: materials ruled-out as candidates for liquid crystallinity at atmospheric pressures may, in fact, be driven into ordered phases at elevated pressures. Moreover, as elevated pressures are routine during polymer processing, no additional complications are required for practical application of this finding. Finally, the evidence of a pressure-induced crystalline phase, confirmed by the X-ray, reveals that the pressure dependent morphological changes in thermotropic copolyesters could be very significant.

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FIGURE CAPTIONS

Figure 1. Room temperature x-ray scattering intensity vs. 2θ of HIQ-20 samples subjected to different pressures and temperatures in the mesophase; all samples were annealed for 1 hour at the respective conditions: A, $P = 1$ bar (330°C); B, $P = 100$ bar (333°C); C, $P = 200$ bar (335°C); D, $P = 300$ bar (337°C).

Figure 2. Wide angle x-ray powder diffraction patterns of the HIQ-20 low pressure crystal form (K1) and high pressure crystal form (K2).

Figure 3. DSC traces of HIQ-20 K1 and K2 crystal forms, using a heating rate of $10^\circ\text{C}/\text{min}$. A, K1 (first run); B, K2 (first run); C, K2 (second run, after specimen was cooled at $10^\circ\text{C}/\text{min}$ at 1 bar).

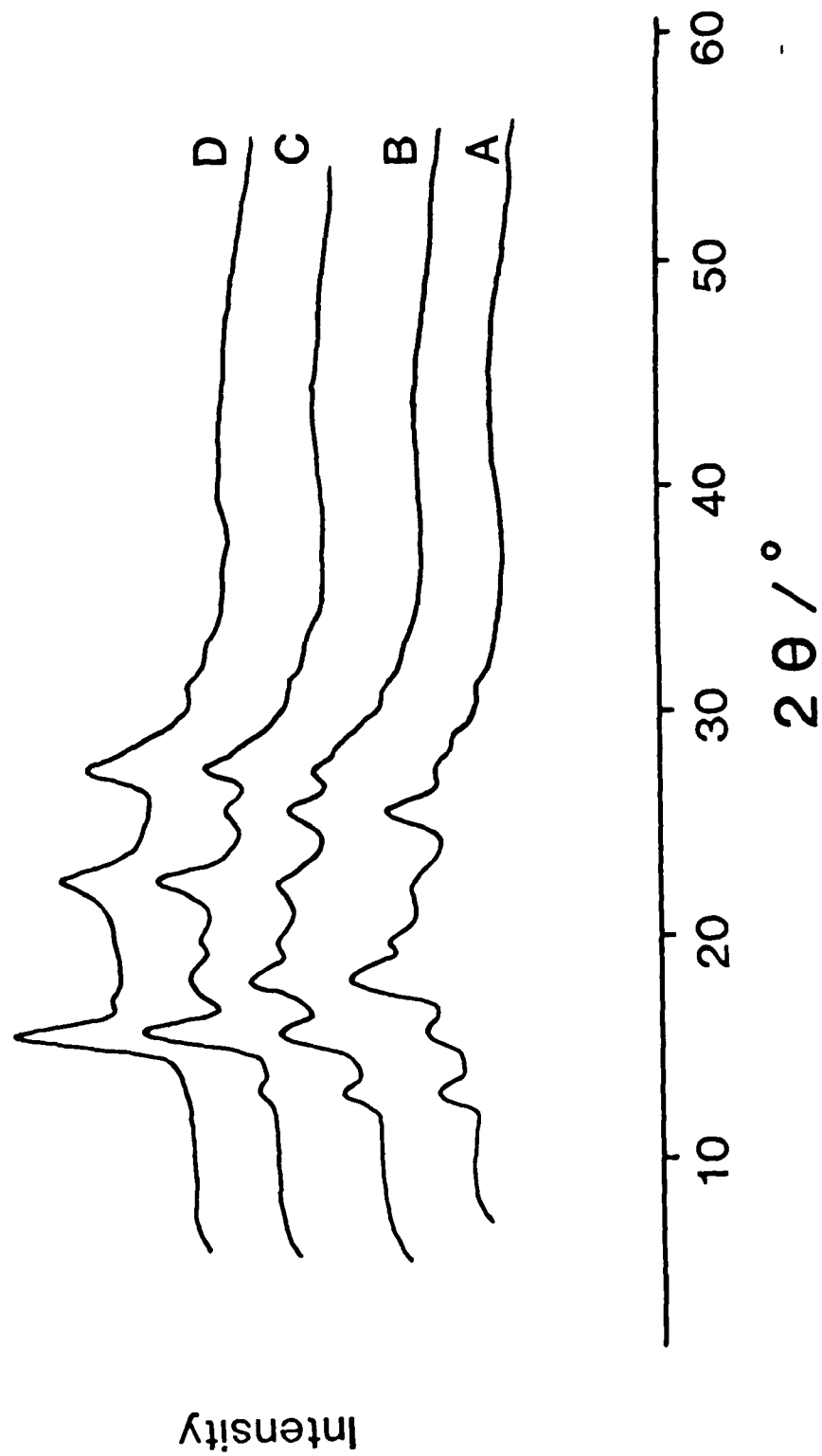
Figure 4. High pressure (1000 bar) DTA traces of HIQ-20 at a heating rate of $3^\circ\text{C}/\text{min}$. A, K1 and K2 mixture; B, K2 sample.

Figure 5. Proposed phase diagram for HIQ-20. Solid line, phase boundaries checked by Clapeyron equation; dotted line, proposed phase boundaries; K1, low pressure crystal form; K2, high pressure crystal form; M1, mesophase 1; M2, mesophase 2; I, isotropic.

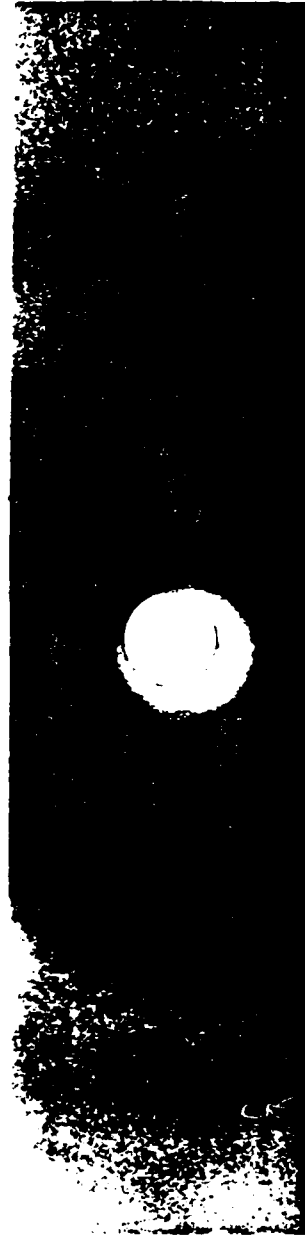
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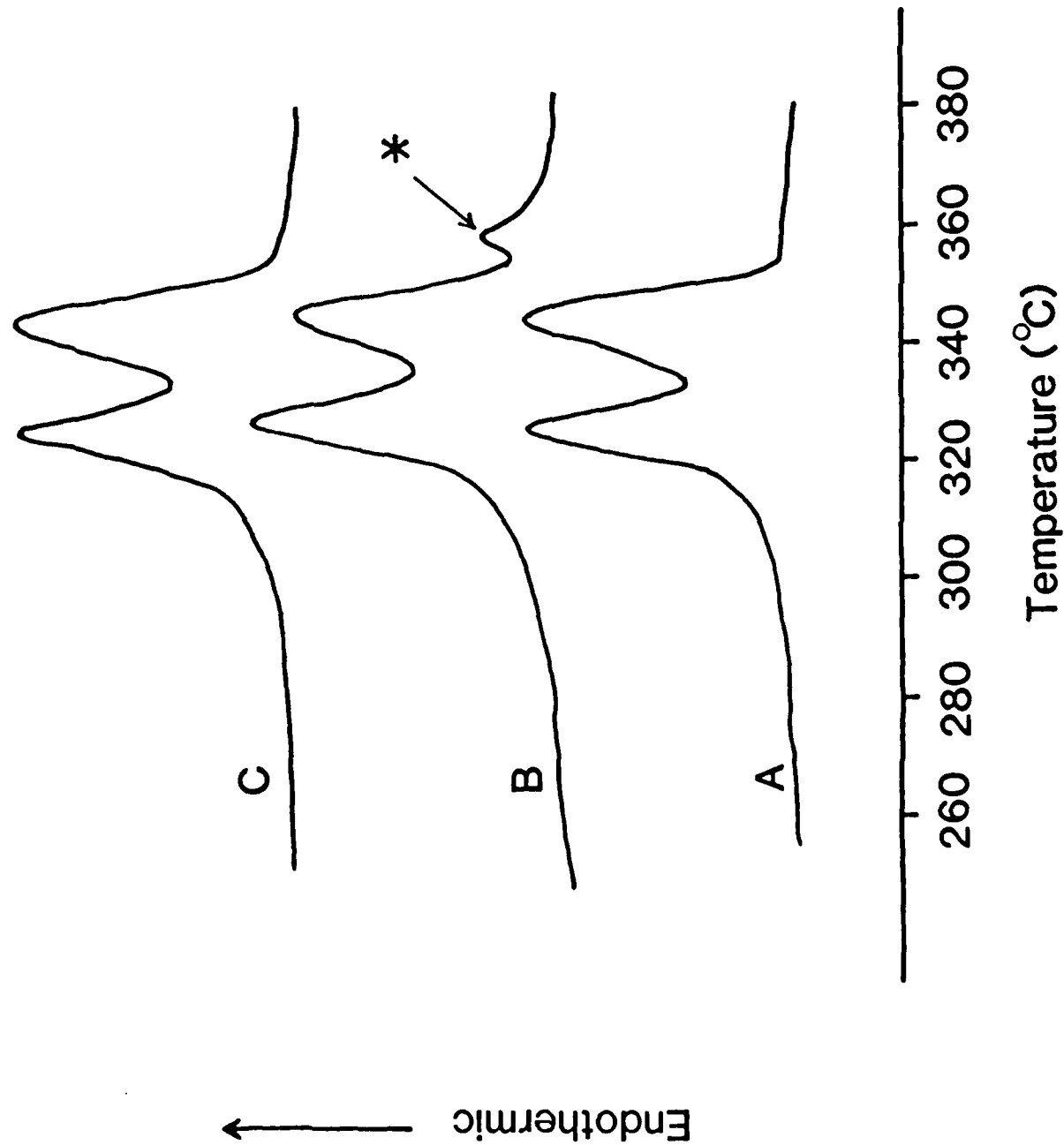


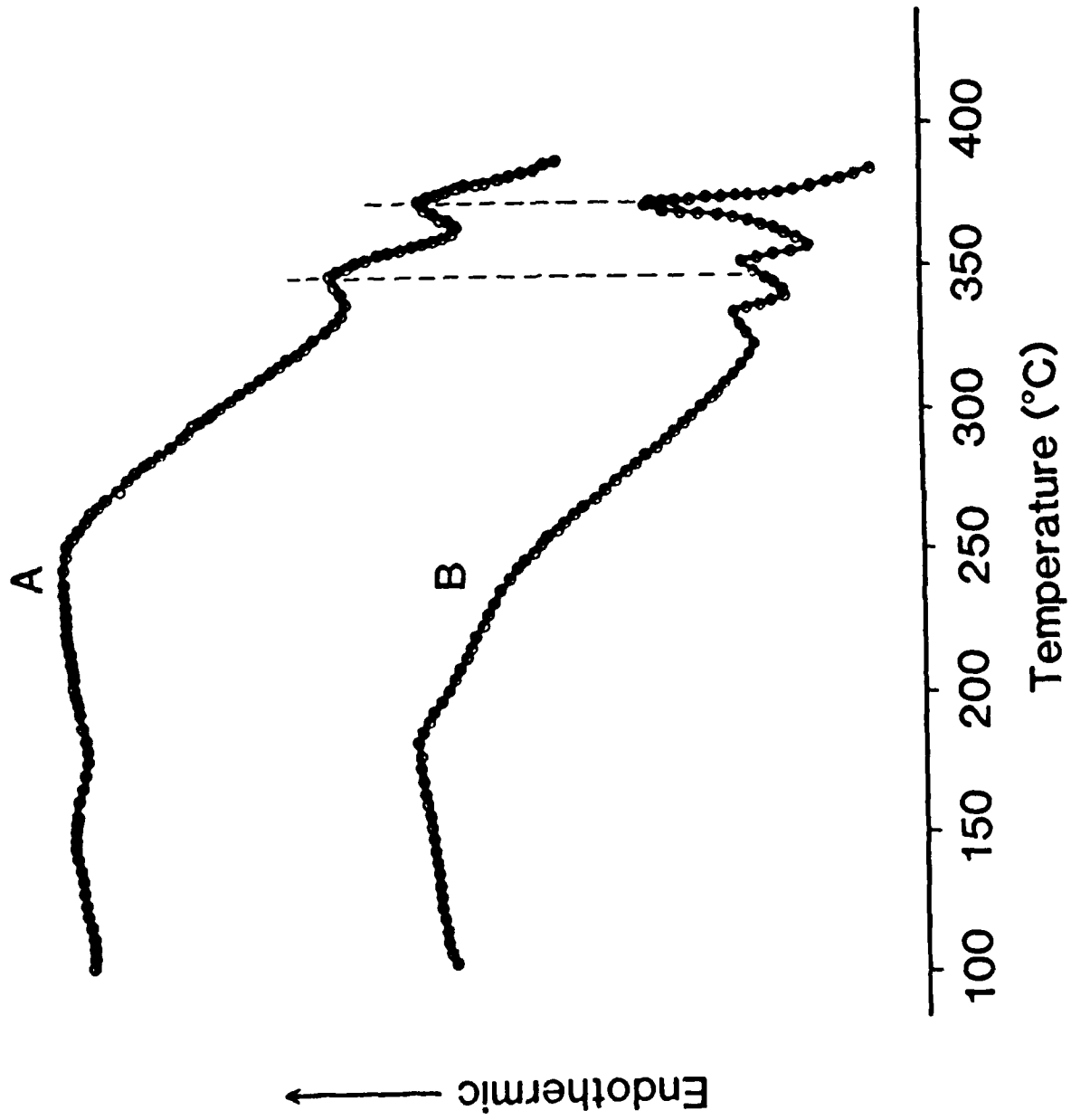
Low Pressure Crystal form

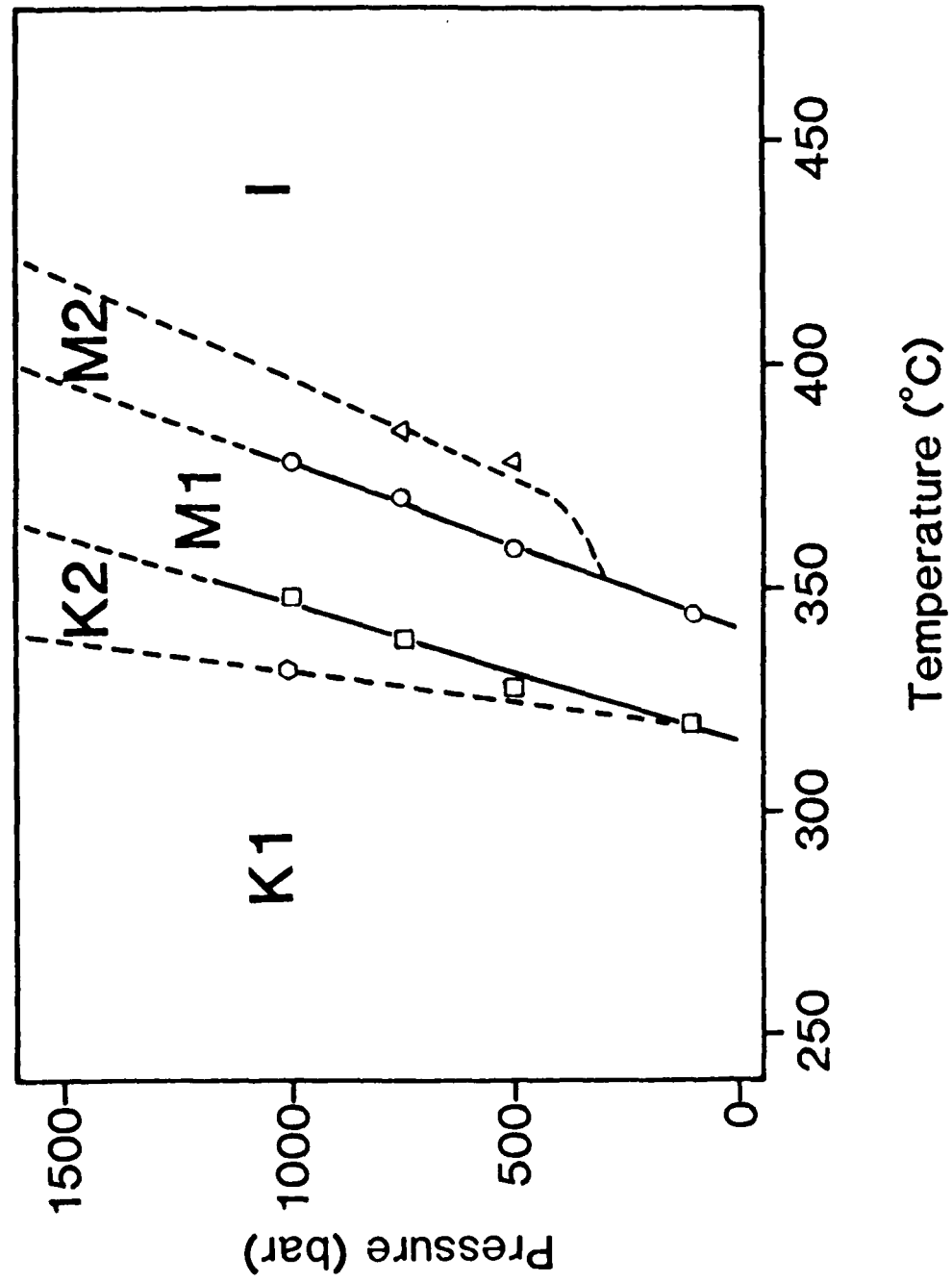


High Pressure Crystal form









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