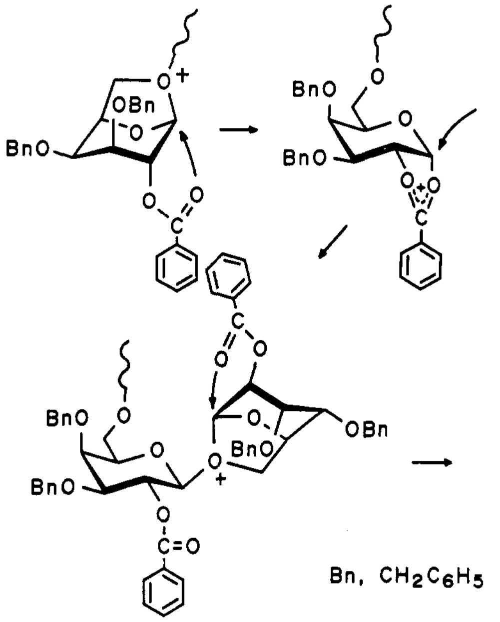
Scheme II
Neighboring Group Participation in the Ring-Opening Polymerization of 1,6-Anhydro-2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-galactopyranose (1)



of (1→6)-α-D-galactopyranan[13,14] was detected,. The area ratio of the central C-1 and nonreducing C-1 signals gave a $\overline{\mathrm{DP}}_n$ value of 7.

Scheme II illustrates the proposed mechanism of neighboring group participation in the polymerization of 1. The trialkyloxonium ion is transiently formed at the growing terminal unit,[9] but it is immediately attacked by the carbonyl oxygen of the neighboring benzoyl subistituent with inversion of the C-1 configuration to form a dioxacarbenium ion (or benzoyloxonium ion). As a result, the incoming monomer can attack the reaction center exclusively from the opposite side of the dioxacarbenium ion, that is, the β-side of the pyranose ring, and the trialkyloxonium ion is regenerated. The relatively stable dioxacarbenium ion is responsible for the lower reactivity of 1 compared to the tribenzylated analogue.

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Pressure-Induced Phases in a Thermotropic Polyester

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 a copolyester of 20% hydroxybenzoic acid, 40% isophthalic acid, and 40% hydroquinone, "HIQ-20", whose composition lies just inside of the mesophase range. This work was motivated by observations that low molar mass (isotropic) liquids may be transformed into mesophases at elevated pressures.[1] Pressure-induced liquid crystallinity is simply a consequence of the reduced molar volume (relative to the isotropic state) that characterizes fluids having long-range orientational order. Chandrasekhar et al.[2] have reviewed this phenomenon in low molar mass liquid crystals. Pressure effects in LCPs have also been investigated.[3]

As anticipated, we find that at elevated pressure, the previously reported mesophase of HIQ-20 persists over a wider temperature range, but also, a second high-temperature mesophase is induced at elevated pressure. 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 cooled at ambient pressure. This observation is particularly noteworthy because the pressure required for forming the new solid morphology is comparable to or less than pressures employed in conventional processing techniques.

A rheological investigation and brief description of the synthesis of HIQ copolyesters at various HBA compositions has been recently reported by Kiss.[4] We confirmed by hot-stage optical microscopy and DSC that HIQ-20 exhibits a mesomorphic phase consisting of a melting transition (crystalline to mesomorphic) at 324 °C and a clearing transition (mesomorphic to isotropic) at 342 °C. 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 (0.6 GPa). A detailed description of this apparatus, which was also used to prepare HIQ-20 specimens annealed and solidified at various pressures, has been given previously.[5]

The X-ray 2θ-scans of HIQ-20 specimens prepared at different pressures show significant differences, indicating that the structure in the solid state changes with the pressure applied during annealing and cooling. At atmospheric pressure the normally observed crystalline phase

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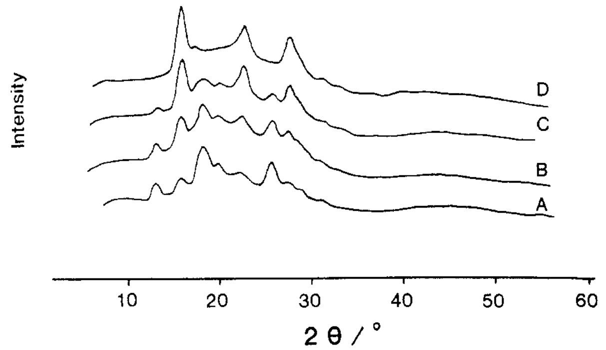

Figure 1. Room temperature X-ray scattering intensity versus 2θ of powdered HIQ-20 samples annealed at different pressures and temperatures in the mesophase then cooled (under pressure) into the solid state; all samples were annealed for 1 h at the respective conditions: (A) P = 1 bar (330 °C); (b) P = 100 bar (333 °C); (C) P = 200 bar (335 °C); (D) P = 300 bar (337 °C). Normalized 2θ-scans were derived from the X-ray films (a Debye–Scherrer camera with Ni-filtered Cu Kα radiation) with an Optronics Model 1700 densitometer.

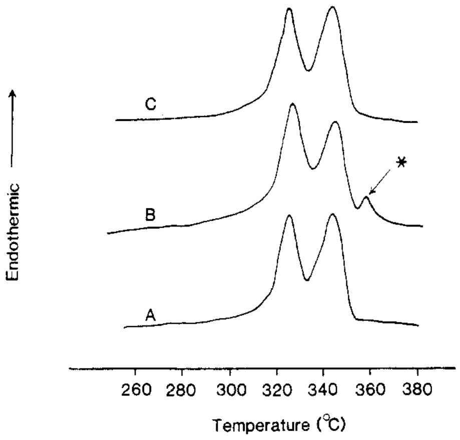

Figure 2. DSC traces of HIQ-20 samples in the K1 and K2 crystal forms, using a heating rate of 10 °C/min: (A) K1 (first run); (B) K2 (first run); (C) K2 (second run, after specimen was cooled at 10 °C/min at 1 bar).

K1 is formed (Figure 1A); the K1 structure is independent of the thermal history.[6] When the pressure is increased, K1 is lost in favor of a new pressure-induced structure, a crystal form designated K2 (Figure 1B–D). The minimum pressure required to convert from K1 to K2 is approximately 300 bar; between 1 and 300 bar, the X-ray data indicate a mixture of K1 and K2 crystal habits. The 2θ-scan is independent of pressure between 300 and 2000 bar.

The DSC traces of K1 and K2 samples are shown in Figure 2. The first heating curve of the K2 sample exhibits an additional endothermic transition which disappears in the second scan. 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 one another. The DTA thermogram at high pressure exhibits multiple transitions, the lowest of which is probably to be associated with a K1 to K2 transition.[6] The pressure-induced endothermic transition in the high-temperature region in Figure 2 is attributed to a new mesophase, M2, as distinct from the original mesophase, M1. The pressure dependence of these transitions is summarized in a proposed phase diagram of HIQ-20 shown in Figure 3. All data points were obtained from high-pressure DTA. The solid lines have been checked with Clapeyron equation by using P–V–T data;[6] the broken lines are proposed phase boundaries.

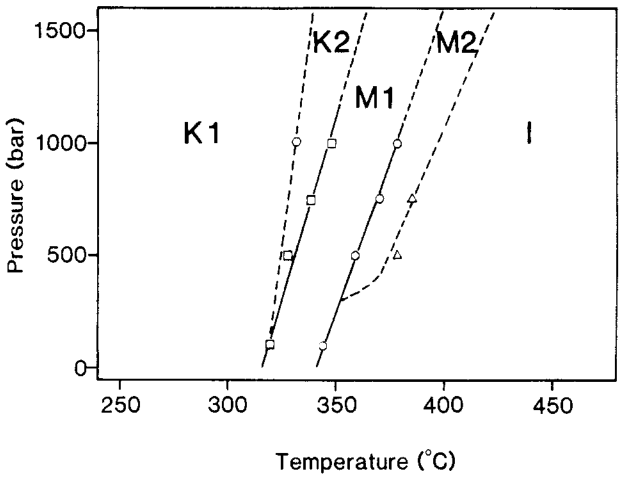

Figure 3. Proposed phase diagram for HIQ-20. The solid lines are phase boundaries checked by Clapeyron equation; the dotted lines are proposed phase boundaries: K1, low-pressure crystal form; K2, high-pressure crystal form; M1, mesophase 1; M2, mesophase 2; I, isotropic.

It is suspected that in the HIQ copolyesters, HBA stiffens the polymer and imparts mesomorphism while IA/HQ sequences are less ordered and promote isotropic phases.[4] There is also evidence that these two structurally different components may drive microphase segregation, namely, an HBA-rich mesomophase and a HBA-depleted isotropic phase.[7,8] If pressure induces segregation of HBA-rich domains in HIQ-20, one might expect to see an X-ray diffraction pattern characteristic of the HBA homopolymer. However, there is no evidence for diffraction characteristic of the crystalline HBA homopolymer in either the K1 or the K2 forms.[9-11] HIQ-20 may very well be a random copolyester with a random primary structure like that found in HBA/2-hydroxy-6-naphthoic acid (HNA) copolyester.[12-14] Furthermore, all thermal transitions observed in HIQ-20 are reversible, indicating no substantial transesterification and associated block formation in the primary structure during sample preparation.[15,16]

We are not able to confirm with optical microscopy the structure of M1 (nematic or smectic). (A smectic phase would imply long-range lateral interactions confined to layers orthogonal to the chain axis.) Specimens quenched from M1 in ice water (at ≈ 100 °C/s) always yielded a K1 crystal structure and there is probably a minimal reorganization of chains on quenching M1. However, it is difficult to extract evidence for interchain translational order from the powder diffraction data. Optical studies indicate that M1 is a highly viscous mesophase; the shear viscosity (η) in HIQ-20 at temperatures in the M1 phase is approximately 10000 P.[17] 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. As for the identification of M2, structural analysis must be carried out at high pressure since efforts to quench M2 always resulted in the K2 structure.

The "HIQ-20" thermotropic polyester is a rather complicated polymorphic system with high transition temperatures and narrow mesophase ranges. Additionally, this polyester exhibits a pressure-induced mesophase at high temperatures (M2) and a pressure-induced crystal phase (K2). Generally speaking, these findings indicate that it may be possible to broaden the range of materials (copolyester composition) that will form mesogenic polymers: materials ruled out as candidates for liquid crystallinity at atmospheric pressures may be driven into ordered phases at elevated pressures. (Similarly, flow fields may also induce liquid crystallinity in isotropic polymer solutions.[18]) Moreover, as elevated pressures are routine during polymer processing no additional complications are required for practical application of these findings. For example, the evidence of a new pressure-induced crystalline phase could have significant potential technological importance in optical storage applications: refractive index changes are expected to parallel changes in density, and changes in the latter quantity might be achieved locally by initiating the transformation K2 → K1 via laser irradiation.

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Registry No. (HQ)(HBA)(IA) (copolymer), 112482-60-7.

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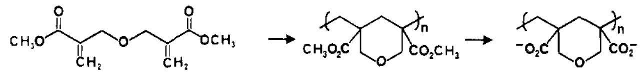
Cyclopolymerization of the Ether of Methyl α-(Hydroxymethyl)acrylate

We have elsewhere reported the synthesis, purification, and characterization of several ethers and acetals of methyl α-(hydroxymethyl)acrylate.[2] We have also reported their use as cross-linking agents in the polymerization of various vinyl monomers including hydrolysis of **1** to the dicarboxylate and its use in cross-linking water-soluble and water-dispersible monomers.[3] While bulk and solution polymerization of **1** generally leads to insoluble and highly cross-linked products,[2] we have discovered conditions leading to soluble polymer of structure **2**. We here report the synthesis and characterization of this new polymer and its partial hydrolysis to the water-soluble derivative **3**.



1 2 3

Radical and photoinitiated bulk polymerization and radical solution polymerization of ether **1** in dimethyl sulfoxide gave only insoluble products. Anionic polymerization has so far been unsuccessful in tetrahydrofuran and toluene with *n*-butyllithium as initiator. However, when a 3% benzene solution of **1** was polymerized with 2,2′-azobis(isobutyronitrile) at 60 °C, polymer precipitated that was subsequently soluble in chloroform and methylene chloride. Reprecipitation into ether gave cyclopolymer **2** as a white powder having a melt/decomposition temperature of 270–275 °C. DSC confirmed the melting transition at 270 °C and also showed a strong glass transition temperature at 160 (onset) or 165 °C (midpoint). Intrinsic viscosity of this polymer was found to be 0.43 dL/g in $CHCl_3$ at 25 °C. Polymerization was also successful in acetone, although both acetone and benzene gave insoluble material along with the soluble fractions. Chloroform gave good conversion to soluble polymer with viscosities of 0.15–0.45 dL/g.

The IR spectrum of **2** showed two distinct carbonyl peaks centered at 1752 cm^{-1} possibly corresponding to cis and trans carboxymethyl groups on the six-membered ring repeat units.[4] Strong ether and ester bands were observed at 1150 and 1270 cm^{-1}, respectively. The ^{1}H NMR spectrum contained only broad, overlapping peaks consistent with the proposed structure. The ^{13}C NMR spectrum is given in Figure 1. Peak assignment is based on comparison to monomer and model polymers as well as on the fully coupled spectrum also shown. The carbonyl carbons show a multiplicity which may be due to tacticity and/or cis/trans ring substitution. No residual unsaturation due to pendent vinyl groups was observed in the IR and NMR spectra of reprecipitated samples.

Cyclopolymer **2** was hydrolyzed under heterogeneous conditions in a 1:1 mixture of methanol and water containing 5% NaOH at 65–75 °C overnight. Dissolution during reaction gave a viscous polymer solution which was then acidified to precipitate the poly(carboxylic acid) polymer. The precipitated polymer was subsequently soluble in aqueous base. The IR spectrum of this material showed strong, broad peaks at 3350 and 1770 cm^{-1} attributed to the free acid groups. ^{13}C NMR in dilute base (see the figure) showed a greatly reduced peak for the ester methyl carbon and two peaks for the carbonyl groups, corresponding to hydrolyzed (downfield) and unhydrolyzed ester units. The ratio of these latter two peaks was approximately 3:1 indicating ca. 75% hydrolysis. Further work is under way to increase this to 100% and to completely characterize these polymers.

Proposed structure **3** is similar in overall composition to that of the pyran copolymer **4** obtained from the 2:1 copolymerization of divinyl ether and maleic anhydride,[5]