## Notes

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### Inverse gas–liquid chromatography for detection of order–disorder in poly(vinyl chloride)

Several reports of order–disorder phenomena occurring through various temperature regions have been made for poly(vinyl chloride) (PVC) and other polymers using spectroscopic methods[1–7], inverse gas–liquid chromatography (IGLC), and conventional differential scanning calorimetry (DSC)[8–10]. Our work with the IGLC method sensitively detects structural variations apparently related to the order–disorder phenomenon.

The "molecular probes" described by STEIN AND GUILLET[11] have been useful for the detection of $T_g$ with the IGLC method by detection of slope changes in plots of specific retention volumes *versus* $1/T$. Our work utilizes a simple *cis/trans* isomer separation to monitor the $T_g$ transition region in a rapid, easily detectable manner, as well as detecting another possible transition. Our differential infrared data supported the IGLC data.

The capability to monitor such variations in polymer systems is constantly being developed by diverse techniques. Although IGLC has been previously utilized for structure studies[11–14], the specific application to PVC using the inherent sensitivity of these certain chromatographic parameters for selected isomers has not been widely developed[15–23].

#### EXPERIMENTAL

A gas chromatographic support, Chromosorb W, high purity, 60–80 mesh, was obtained from Supelco Co., Bellefonte, Pa. PVC was dissolved in tetrahydrofuran and slurried with the Chromosorb W for uniform coating and rotary vacuum dried. The chromatographic columns, 6 ft × 1/4 in. aluminum, were packed to provide a helium flow of *ca.* 30 ml/min for both a 10% by wt. and a 15% by wt. PVC-coated supports. Decalin was obtained as a *ca.* 45/55 mixture of the *cis* and *trans* isomers from Eastman Organic Chemicals, Rochester, N.Y. and used as received. Chromatographic parameters of retention time and resolution were determined in the usual manner for the *cis/trans* decalin solutes.

The application of IGLC to the detection of nematic liquid–crystal transitions was made by DEWAR AND SCHROEDER[15] for a known liquid crystal, *p*-azoxyanisole, using *p*- and *m*-chlorotoluenes as "probes". The known nematic temperature range is 120° to 135°, the temperature region where the observable separation of the toluene species was distinctly and sensitively affected by the liquid crystal changes. NARDI[2] presented evidence for the existence of such non-crystalline (nematic) order in PVC using infrared and X-ray diffraction data. The comparative data from

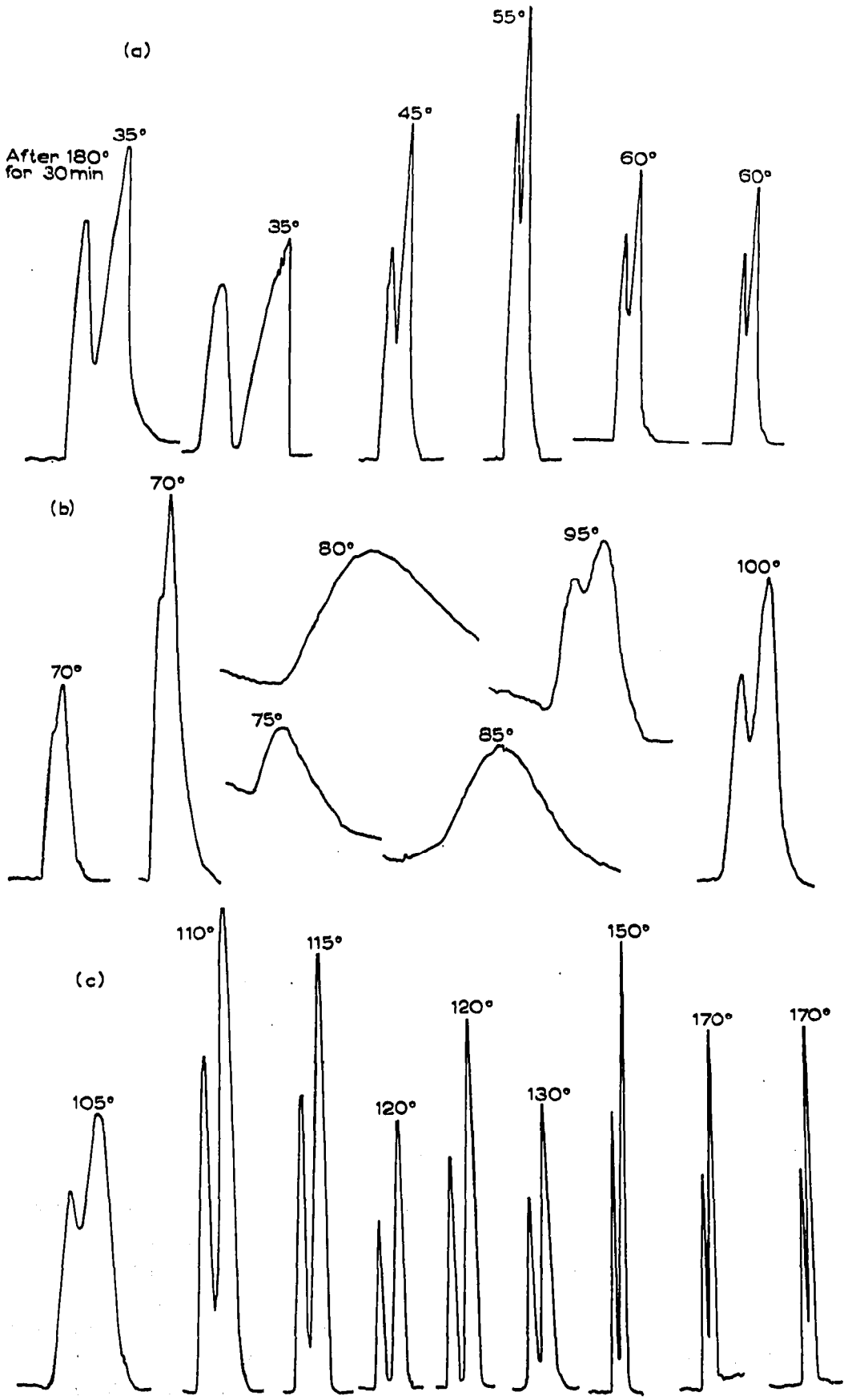


Fig. 1. Inverse gas chromatography of *cis*- and *trans*-decalins on a 15% PVC on 60–80 mesh Chromosorb W column. (a) 35° to 60°; (b) 70° to 100°; (c) 105° to 170°.

the IGLC method on a known liquid-crystal by DEWAR AND SCHROEDER suggested that our IGLC data on PVC substantiates NARDI's contention of nematic order obtained by more conventional methods.

In our work, PVC was deposited as a thin film on Chromosorb W and changes in the chromatographic separation of probes, *cis*- and *trans*-decalins, were recorded (Figs. 1 and 2). Variations in separation and resolution for these two isomers on this substrate are seen in Fig. 3. A dramatic loss of separation and resolution is seen at the $T_g$ range 80 to 95°, with additional discontinuity noted at ~ 105 to 115°. This is the same region as NARDI's detected transition (temp. 105°). The retention time likewise reflects these transitional regions. A column prepared with 10% PVC on Chromosorb W gave essentially the same results. Apparently, IGLC is responsive to changes in order–disorder phenomena directly or indirectly and is able to detect such transitions designated as $T_{1,1}$ (ref. 1), in addition to the well-known $T_g$ transition.

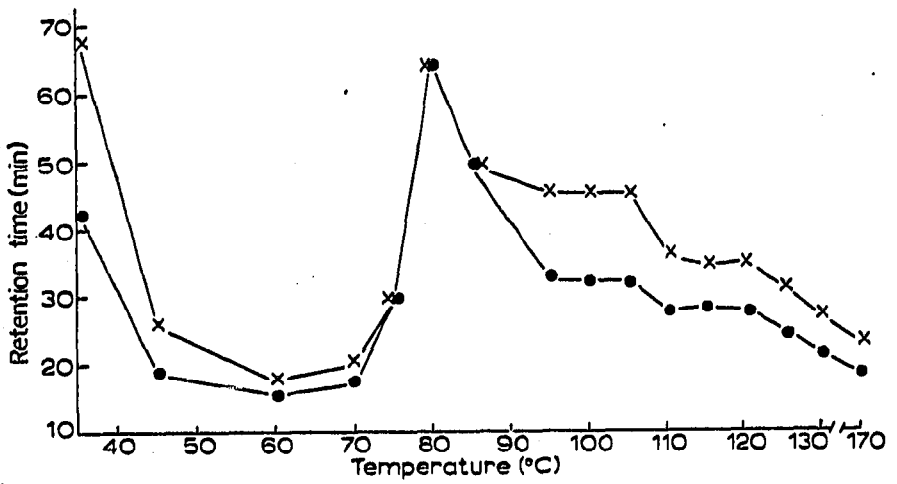


Fig. 2. Retention times for *cis*- and *trans*-decalins as a function of temperature obtained by inverse gas chromatography on a 15% PVC on 60–80 mesh Chromosorb W column. ×, Retention time of *cis*-decalin; ●, retention time of *trans*-decalin.

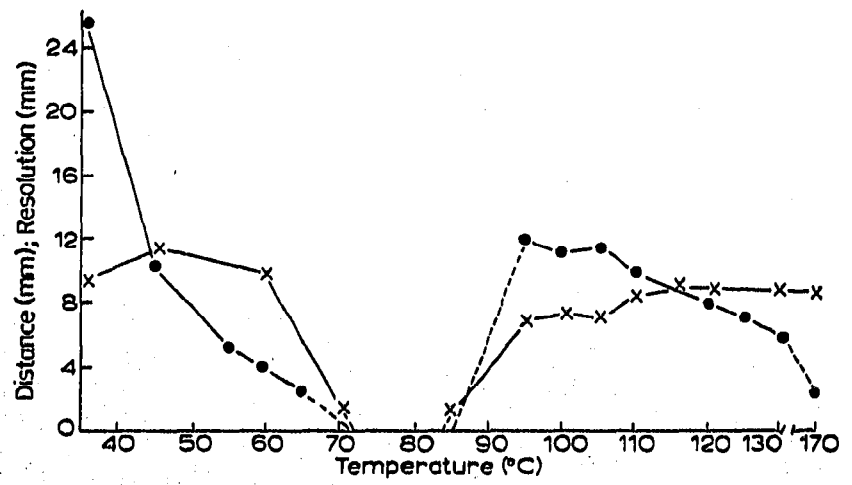


Fig. 3. Separation and resolution of *cis*- and *trans*-decalins as a function of temperature. Gas chromatography was carried out on a 15% PVC on 60–80 mesh Chromosorb W column. ●, Separation; ×, resolution, $R = 2(t_2 - t_1)/(w_1 + w_2)$.

When the IGLC method was used with a chromatographic column of 10% PVC + 3% dioctyl phthalate, behavior of the decalin peaks was monitored throughout the temperature range 75–130°. The separation of the two peaks was maintained, and therefore, the obvious detection of the $T_g$ and the apparent $T_{1,1}$ transition regions were lost. Alternatively, the lack of occurrence of such order–disorder phenomena when plasticizer is present is likely responsible for the experimental observations. DSC was utilized to determine the $T_g$ at 81° for PVC Diamond 450 (with no plasticizer) deposited on Chromosorb W HP for both 10% and 15% by wt. PVC columns. However, when 3% dioctyl phthalate was present in the 10% PVC coating, DSC showed no $T_g$ in that temperature region.

The significance of the IGLC method of analysis to assess polymer–plasticizer interactions, influence of polymer structure, and relaxation phenomena will be studied in greater detail.

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