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# Head to Head Polymers

## 20. DSC Analysis of Blends of Head-to-Head or Head-to-Tail Poly(Vinyl Chloride) with Poly(ε-Caprolactone)*

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## ABSTRACT

Blends of poly(ε-caprolactone) with either head-to-head or head-to-tail poly(vinyl chloride) were prepared by solvent casting in the form of films and their glass transition temperatures were determined by DSC analysis. The DSC scans of the blends of both poly(vinyl chloride) isomers were very similar. For blends containing 25% and 50% of poly(ε-caprolactone), a single transition step, a $T_g$, was observed, whereas for a blend containing 75% of poly(ε-caprolactone) three transition steps were observed, one glass transition and also a crystallization and a melting transition.

## INTRODUCTION

Polymers which have exclusively head-to-head (H-H) linkages are receiving increasing attention since they have become more and more available (MALANGA, et al. 1982). At present H-H polymers can only be prepared by indirect routes. Depending upon the class of H-H polymers, various different procedures for their preparation have been developed. Some of these have been reviewed recently (VOGL, YOSHIDA 1980).

Blends of two or more different homopolymers can result in the formation of materials which have unique properties, not possessed by either of the individual polymers and therefore the determination of the miscibility of polymers has been increasingly studied. Blends of atactic head-to-tail polystyrene (H-T PSt) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been found to be completely miscible over the whole range of compositions and have been successfully commercialized under the trade name of Noryl (HAY 1976). Very recently the investigation of blends with H-H polymers as one of the components has been undertaken. H-H PSt, synthesized in this laboratory (INOUE, et al. 1977) was found to be compatible in blends with PPO over the whole composition range as judged by single $T_g$'s (KRYZEWSKI, et al. 1982). Compatibility of blends of two homopolymers of rather different chemical structure is more likely to be the exception than the norm.

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* Part 19: H. Kawaguchi, J. Muggee, Y. Sumida and O. Vogl, Polymer (London), in press

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Even homopolymers of closely related molecular structures may form incompatible blends.

Miscibilities and glass transition temperatures of mixtures of H-T poly(vinyl chloride) (H-T PVC) with poly($\varepsilon$-caprolactone) (PCL) have been investigated previously by determining their dynamic mechanical properties with a torsion pendulum (KOLESKE, LUNDBERG 1969). It was the purpose of this work to investigate the compatibility behavior of blends of H-H PVC with PCL and to compare it with the compatibility of mixtures of H-T PVC and PCL by DSC analysis. The synthesis of H-H PVC (BAILEY, et al. 1964) by completely chlorinating the double bonds in cis-1,4-polybutadiene has been studied in detail in our laboratory (KAWAGUCHI, et al. 1982) and the chlorination products have been characterized (KAWAGUCHI, VOGL 1982).

## EXPERIMENTAL PART

### Materials

H-T PVC was a commercial product (Montedison, S.p.A., Milan, Italy), $\eta_{inh}$ (THF, 0.5 g/dL, 30°C) = 0.94 dL/g. H-H PVC was prepared in this laboratory (KAWAGUCHI, et al. 1982), $\eta_{inh}$ (THF, 0.5 g/dL, 30°C) = 4.17 dL/g. Before blending, both H-T and H-H PVC were stabilized by treating the polymers with triethylaluminum (THAME, et al. 1972). Tetrahydrofuran (THF) and poly($\varepsilon$-caprolactone) (PCL) (Aldrich Chemical Co.) were used as received.

### Measurements

DSC measurements were carried out on a Perkin-Elmer DSC-2 Differential Scanning Calorimeter at a heating rate of 20°C/min. Film samples (5-10 mg) of homopolymers and blends were used for the DSC studies. The mid-point of the step change associated with the glass transition was defined as the $T_g$.

### Preparation of Films

H-T PVC was dissolved in THF (5%) with stirring, the solution was poured into a flat dish and the solvent was allowed to evaporate at room temperature. Films of H-H PVC were prepared in a similar manner from 2.5% solutions.

Films of the blends were prepared by dissolving appropriate amounts of PVC and PCL (100 mg combined) in THF (5 ml), pouring the solutions into flat dishes and allowing the solvent to evaporate at room temperature.

## RESULTS AND DISCUSSION

The thermal behavior of series of blends of H-H PVC with PCL and H-T PVC with PCL showed only one glass transition in DSC scans in the temperature range between 150 and 400 K. PCL is a highly crystalline polymer with the degree of crystallinity depending upon the history of the sample (KOLESKE, LUNDBERG 1969). PCL has a $T_m$ of 333 K; the $T_g$ is affected by the crystallinity and will occur around 210 K. Our samples had a $T_g$ of 207 K as shown by the DSC scan (Figure 1); by extrapolating dynamic mechanical measurements of PCL blends, 202 K was determined to be the true $T_g$ of completely amorphous PCL (KOLESKE, LUNDBERG 1969).

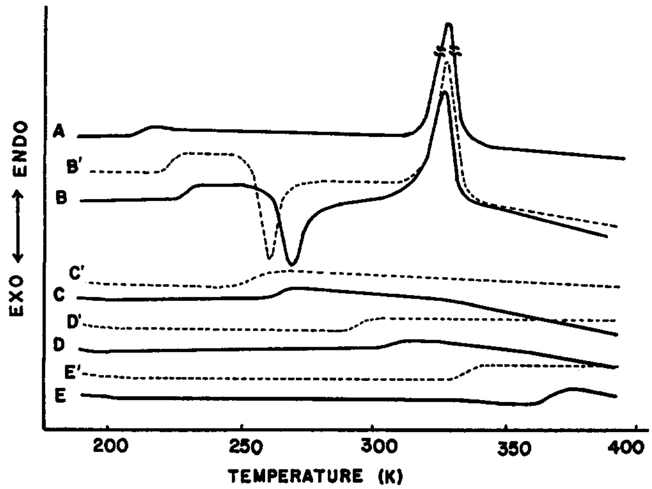

FIGURE 1. DSC Scans of Blends of H-H Poly(vinyl chloride) (—) and of H-T Poly(vinyl chloride) (---) with Poly(ε-caprolactone). A: PCL, B: PVC/PCL = 25/75; C: PVC/PCL = 50/50; D: PVC/PCL = 75/25; E: PVC

Our H-H PVC sample had a $T_g$ of 365 K and the H-T PVC had a $T_g$ of 331 K. The DSC scans of the two sets of PVC blends with PCL were very similar (Figure 1). If the content of PCL in the blend was 25% or 50% only one glass transition and no crystalline melting point was observed in the scans (Table 1). This indicates that PVC disrupts the crystal structure of PCL completely and complete miscibility of the two homopolymers results.

## TABLE 1

Glass Transition Temperatures of Blends of H-H Poly(vinyl chloride) and of H-T Poly(vinyl chloride) with Poly( ε-caprolactone)

| PVC (% w/w) | $T_g$ (K) | |
|---|---|---|
| | H-H PVC | H-T PVC |
| 100 | 365 | 331 |
| 75 | 303 | 287 |
| 50 | 261 | 248 |
| 25 | 229 | 223 |
| 00 | 207 | 207 |

The DSC scans of blends containing 75% PCL were very different. Although they too showed only one glass transition, they also showed an exothermic and an additional endothermic transition step, indicating a crystallization exotherm, and as the temperature increased, a melting endotherm. The blend of H-H PVC with PCL showed a $T_g$ of 229 K, a $T_{cryst}$ of 268 K and a $T_m$ of 333 K; the blend of H-T PVC with PCL showed a $T_g$ of 223 K, a $T_{cryst}$ of 261 K and a $T_m$ of 333 K which is the same as the $T_m$ of PCL itself.

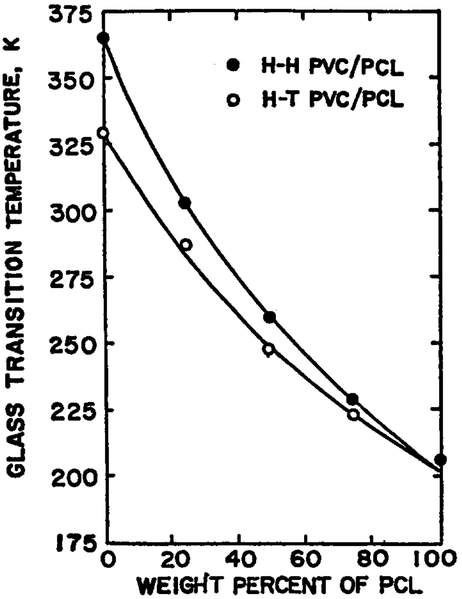

FIGURE 2. Glass Transition Temperature for H-H PVC/PCL and for H-T PVC/PCL Blends as a Function of Composition. The curves were drawn from: $1/T_g = W_1/T_{g1} + W_2/T_{g2}$ where $T_{g1}$ = 202 K, $T_{g2}$ = 365 K and 331 K respectively (Fox-Flory)

These results suggest that also in this high PCL concentration range both PVC structures form blends with PCL which are compatible at temperatures below about 240 K. This is demonstrated by the single $T_g$ and supported by the excellent fit of the experimentally determined $T_g$'s with the theoretical curve obtained from the Fox-Flory expression if the theoretically determined value of 202 K is used for the $T_g$ of amorphous PCL (Figure 2).

Above 240 K phase separation seems to occur and some of the PCL crystallizes and then melts as the $T_m$ of PCL is reached. Koleske and Lundberg had reached similar conclusions based on the dynamic mechanical behavior of PCL blends with commercial (head-to-tail) PVC. Our experiments showed that the blending behavior of H-H PVC with PCL does not differ significantly from that of H-T PVC.

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