# Preparation and properties of poly(valerolactone)

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(*Received* 14 *July* 1980; *revised* 15 *September* 1980)

A poly(valerolactone) (PVL) sample, having a weight average molecular weight of $33 \times 10^3$ g mol$^{-1}$, has been prepared by an anionic polymerization using butyl lithium as initiator. This sample has a glass transition temperature of 206K and a melting point of 332K. Both of these values are very close to those found for poly(caprolactone) (PCL). PVL, as well as PCL, is miscible with poly(vinyl chloride). X-ray data, stress–strain curves, and dynamic mechanical measurements of PVL are also reported.

## INTRODUCTION

The ring-opening polymerization of unsubstituted lactones leads to polyesters having the general formula $[(CH_2)_x\text{–}COO]_n$ where $x \geqslant 2$. The best known member of this series is poly($\varepsilon$-caprolactone) (PCL) ($x = 5$) since it is miscible with a large number of polymers[1].

However, the lowest member of the series, poly($\beta$-propiolactone) (P$\beta$L) ($x = 2$), is not miscible with poly(vinyl chloride) (PVC)[2] despite the fact that $\alpha$,$\alpha$-substituted poly($\beta$-propiolactones) are[3]. Generally the latter polymers have more interesting properties than their unsubstituted homologues[4].

We considered the properties of other polylactones of the same series with the possibility of using them in blends with PVC or other polymers. Unfortunately, poly($\gamma$-butyrolactone) ($x = 3$) cannot be polymerized, $\gamma$-butyrolactone being too stable[5]. However, poly($\delta$-valerolactone) (PVL) ($x = 4$) can be prepared with high molecular weights. Little is known about the physical properties of this polymer therefore the PVL glass transition temperature, $T_g$, melting point, $T_m$, and enthalpy of fusion, $\Delta H$, will be reported. Dynamic mechanical properties such as storage modulus, $E'$, loss modulus, $E''$, and loss tangent, tan $\delta$, will be presented as a function of temperature. Finally, a PVL–PVC blend will be studied and will be shown to present miscibility in the solid state.

## EXPERIMENTAL

Two PVL samples were polymerized. The first was prepared according to the general procedure described by Cherdron, Ohse and Korte, using a cationic initiator, trifluoroacetic acid. The bulk polymerization was conducted at an initiator concentration of 1 mmol per mole of monomer, at 293K, under a dry nitrogen atmosphere. After three days, a powdered polymer was recovered by washing the solid in suspension in the liquid monomer with anhydrous ether (30% yield). This polymer has a low molecular weight since its intrinsic viscosity, measured in tetrahydrofuran (THF) at 298K, is only 0.174 g dl$^{-1}$ and since films prepared from this sample are very brittle.

The second sample was prepared following the general procedure described by Ito, Tomida and Yamashita[7], using an anionic initiator, butyl lithium. The polymerization was conducted in THF, at a monomer volume concentration of 30%, an initiator concentration of 1 mmol per mole of monomer, 293K, and under a dry nitrogen atmosphere. Within 10 min, the viscosity of the solution increased significantly. After 20 min, the polymer was washed with anhydrous ether, dissolved in benzene, reprecipitated in methanol and dryed in a vacuum oven (90% yield). This second PVL sample was used for all measurements reported in this paper.

This sample has a weight average molecular weight of $33 \times 10^3$ g mol$^{-1}$ and a polydispersity index of 4.8 according to the gel permeation chromatographic analysis. Its intrinsic viscosity, measured in THF at 298K, is 0.50 g dl$^{-1}$. This sample produces hazy films from THF, or when prepared under a laboratory press, due to the crystallinity of the sample. Films were also prepared from dichloromethane which were clearer than those prepared from THF due to their lower degree of crystallinity, verified by calorimetry measurements.

The i.r. spectrum of the polymer presents characteristic absorption bands at 2950 (s), 1760 (s), 1400 (s) and in the region 1300–1000 cm$^{-1}$ (s) (s stands for a strong intensity band).

The nuclear magnetic resonance spectrum of PVL, taken in deuterated chloroform, at ~10% concentration, at 298K and 90 MHz, presents characteristic resonance lines at 1.7, 2.3 and 4.1 ppm. These three bands have an intensity ratio of 4:2:2, and can be assigned to the PVL repeat unit.

X-ray measurements were also conducted on an apparatus comprising a Philips generator equipped with a Statton–Warhus camera[8]. A CuK$_\alpha$ target was used. The camera was calibrated with NaCl crystals. The characteristic lines of the PVL sample are given in *Table 1* in terms of Bragg angles, $2\theta$, intensity, $I$, and interplanar distance, $d$.

For mechanical property measurements, films have been prepared by solvent evaporation, from a $CH_2Cl_2$ solution. The stress–strain measurements were done on an Instron tensile machine, table model 1130. The dynamic measurements were recorded using a Rheovibron DDV-II instrument (Toyo Baldwin Inc.) at frequencies of 3.5, 11, 35 and 110 Hz in a temperature range 130–300K.

0032-3861/81/091223-04$02.00

*Table 1* X-ray data of poly(valerolactone)

| $2\theta$ | $I$ | $d$ (nm) |
|---|---|---|
| 5.9 | M | 1.50 |
| 15.2 | W | 0.58 |
| 17.8 | W | 0.50 |
| 21.5 | VS | 0.41 |
| 24.2 | S | 0.37 |
| 27.2 | S | 0.33 |
| 30.4 | M | 0.29 |
| 38.6 | W | 0.23 |
| 41.2 | W | 0.22 |

VS = very strong; S = strong; M = medium; W = weak

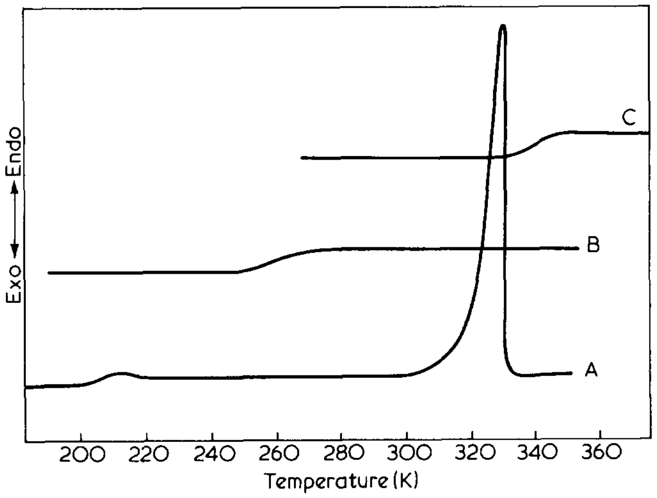

*Figure 1* D.s.c. heating curve at 20 K $min^{-1}$ for (A) PVL, (B) a 50–50% PVL–PVC blend, and (C) PVC

Differential scanning calorimetry (d.s.c.) measurements were made with a Perkin–Elmer DSC-2 apparatus. The instrument was calibrated with gallium and indium at the same heating rate as that used for the polymer.

## RESULTS AND DISCUSSION

### *Thermal properties*

D.s.c. measurements were conducted on PVL samples which were melted in the calorimeter at 370K during 5 min, cooled to 140K at a cooling rate of 360K $min^{-1}$, and then reheated. A typical heating curve is given in *Figure 1A*, showing two well defined transitions. There is a jump in heat capacity at 206K characteristic of a glass transition temperature, and a melting endotherm around 325K. The melting point, $T_m$, defined at the end of the melting curve is 332K. The enthalpy of fusion, $\Delta H$, measured under the melting curve is 63 J $g^{-1}$. The melting curve of *Figure 1A* is relatively sharp as compared to those which are often observed for other polylactones[4]. Its width at half-height is 5K.

Also, other cooling regimes, namely cooling rates of 10, 2.5 and 0.62K $min^{-1}$, instead of 360K $min^{-1}$, did not change the above results significantly. In all cases, $T_m$ was $334 \pm 2$K, $\Delta H$ was $62 \pm 2$ J $g^{-1}$ and the width at half-height was 5–6K.. A PVL film prepared from $CH_2Cl_2$ solution lead to roughly the same values while films prepared from THF lead to increases in $\Delta H$ of the order of 50%. All these values indicate that PVL has a high tendency toward crystallization and that it cannot be quenched easily.

### *Mechanical properties*

A typical stress–strain curve of PVL is shown in *Figure 2*. It shows a yield point at 6% elongation and at 12.5 MPa. For larger elongations, the sample necks and the stress–strain curve is characterized by a plateau at a stress of ~11 MPa up to the rupture, occurring at elongations between 150 and 200%. The Young's modulus of PVL is 0.57 GPa.

Mechanical recovery experiments were also carried out. PVL films were deformed and the residual elongation after the total release of stress was recorded. It was observed that there was no permanent deformation of PVL for elongations up to 2.2%. Permanent deformations of 10 and 15% were seen for 4.0 and 5.0% elongations, respectively. Larger initial deformations lead to important values of permanent deformation.

The Rheovibron measurements at 110 Hz lead to the storage modulus, $E'$, to the loss modulus, $E''$, and to the loss tangent, tan $\delta$, which are shown in *Figures 3* and *4*. The experimental values of tan $\delta$ were corrected according to Massa's equation[9,10]. The $E'$ curve is characterized by three different regions: there is a region of decreasing values of $E'$ at low temperatures, followed by a plateau between 180 and 210K, followed by a decrease in $E'$ at higher temperatures. The $E''$ curve presents a clear maximum at 238K and the onset of a maximum at low temperatures, around 134K. The maximum at 238K in the $E''$ curve, along with the decrease in the $E'$ curve, can be

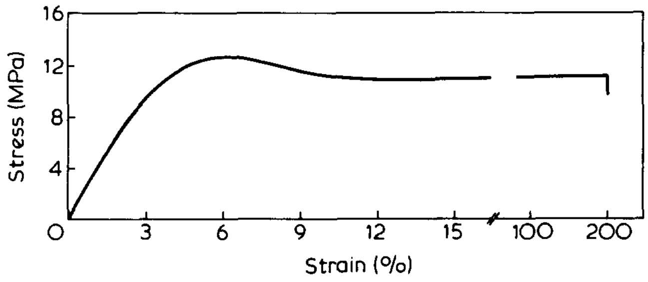

*Figure 2* Stress–strain curve of poly(valerolactone) at 298 K (strain rate = 1% $min^{-1}$)

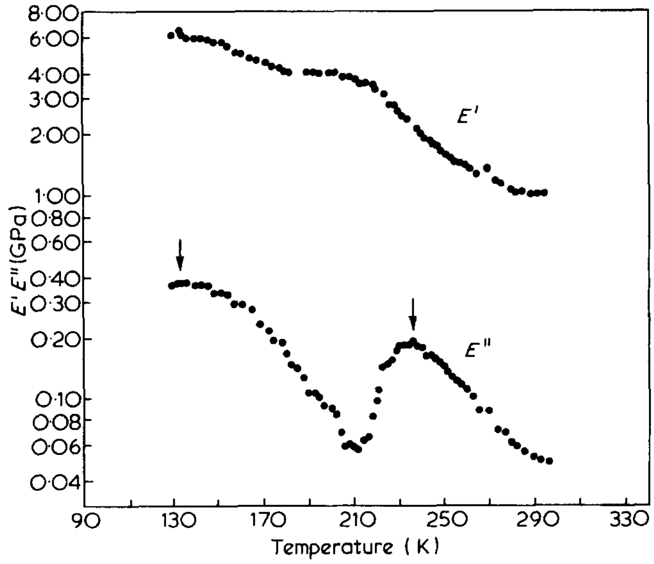

*Figure 3* $E'$, $E''$-temperature dependence of poly(valerolactone) at 110 Hz

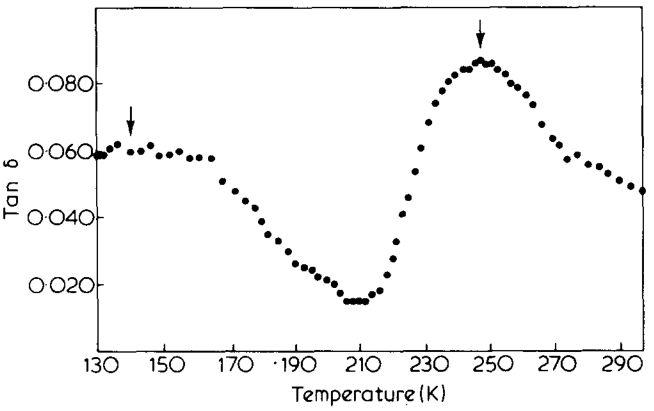

*Figure 4* Tan δ-temperature dependence of poly(valerolactone) at 110 Hz

associated with $T_g$ where an important decrease in $E'$ is expected. The other maximum indicates the presence of a secondary relaxation which must be related to a local deformation of the main chain of the polymer since PVL does not possess any side chain. Such secondary relaxation is also found in PCL and has been ascribed to the motion of the $CH_2$ sequence units generally occurring when three or more methylene units are in sequence[11,12]. Specific mechanisms have been proposed to explain this motion[11-15]. By analogy, it is proposed that the secondary relaxation occurring in PVL is due to a similar motion as that in PCL.

Similarly, the tan δ curve presents a maximum at 246K which can be associated with $T_g$, and an ill defined maximum around 140K associated with the secondary relaxation discussed above. The $T_g$ defined from the tan δ curve is found at a higher temperature than that obtained from d.s.c. since the former experiment was conducted at high frequencies. The tan δ peak at 246K has also an intensity of 0.087 which is normally found for a sample of relatively high degree of crystallinity[4].

For the glass transition temperature process, an apparent activation energy, $E_a$, can be calculated using Arrhenius' equation

$$F = F_0 \exp[-E_a/RT] \qquad (1)$$

where $F$ is the measuring frequency, $F_0$ is the frequency when the temperature approaches infinity, $T$ is the temperature corresponding to a maximum in the tan δ curve at $F$, and $R$ is the gas constant. The least squares method applied to the results obtained for PVL yielded a value of $E_a$ of 215 kJ mol$^{-1}$. This value is of the same order of magnitude as those found for other polylactones[4].

### *PVL–PVC blends*

Finally, a 50–50 weight percent PVL–PVC blend was prepared from $CH_2Cl_2$, submitted to the same thermal history as the PVL sample of *Figure 1a* and run in the d.s.c. The curve of *Figure 1b* was then obtained indicating that the sample presents a single glass transition temperature at 260K, and that it is completely amorphous since no melting curve was recorded. For comparison purposes, the d.s.c. thermogram of the PVC sample used was made and it is presented in *Figure 1c*. In the 50–50 blend, PVC acts as a diluent and it stops completely the crystallization of PVL at least under the thermal regime investigated. In addition, if one accepts the usual $T_g$ criterion for blend miscibility[16,17], the PVL–PVC blend can be declared as completely miscible. A complete analysis of PVL–PVC blends will be presented in a later paper[18].

## CONCLUSIONS

The d.s.c. analysis of PVL, combined with dynamic mechanical measurements, indicate a $T_g$ of 206K and a $T_m$ of 332K. These values can be compared with those of PCL and PβL, as is done in *Table 2*. PVL transition temperatures are very similar to those found by several authors for PCL. But the transition temperatures of PVL and PCL are significantly lower than those found for PβL. The difference in $T_m$ between PCL and PβL has been ascribed to a higher configurational entropy of the PCL chain due to its higher flexibility as compared to that of the PβL chain, and leading to a lower PCL melting point[19]. Similarly, the higher intrinsic flexibility of the PCL chain due to its longer methylene sequence unit ($x = 5$) as compared to that of PβL ($x = 2$) explains the lower $T_g$ of the former. A comparison between PVL and PCL transition temperatures indicates that in polylactones, the difference brought about by shortening the methylene sequence length from five units to four, is negligible. The PVL molecule probably has similar intrinsic flexibility and similar configurational entropy than PCL.

*Table 2* shows that the melting point observed for PVL agrees with that found by Chatani *et al.*[26]. It is slightly larger than those reported by Carothers[24,25]. The difference being due to the high molecular weight of our sample compared to those of Carothers.

*Table 2* also shows a small disagreement in the literature about the $T_g$ of PβL. A possible explanation would be differences in molecular weights of the PβL samples used. Crescenzi *et al.* studied samples having molecular weights larger than 50000 g mol$^{-1}$ [19]. We used a PβL having a molecular weight of ~10000 g mol$^{-1}$, and got a lower value than Crescenzi *et al.*[20]. The low value obtained by Coleman and Varnell is probably due to a low molecular weight sample.

The $\Delta H$ for PVL from *Figure 1a* is close to the $\Delta H$ obtained for PCL when prepared under similar conditions. Assuming that the enthalpy of fusion of the PVL crystal is close to that of the PCL crystal, a $\Delta H$ of 63 J g$^{-1}$ would lead to a degree of crystallinity of 45%.

Finally, the d.s.c. measurements indicate complete miscibility between PVC and PVL in a 50–50 mixture.

*Table 2* Comparison of the transition temperatures, $T_g$ and $T_m$, for $\text{+}(CH_2)_x\text{–}COO\text{+}_n$ polymers

| Polymer | Repeat unit | $T_g$ (K) | $T_m$ (K) | Reference |
|---|---|---|---|---|
| Poly(β-propiolactone) | $\text{+}(CH_2)_2\text{–}COO\text{+}_n$ | 258 | 357 | 19 |
| | | 250 | 357 | 20 |
| | | 200 | 350 | 2 |
| Poly(δ-valerolactone) | $\text{+}(CH_2)_4\text{–}COO\text{+}_n$ | 206 | 332 | This work |
| | | – | 326 | 24 |
| | | – | 328 | 25 |
| | | – | 333 | 26 |
| Poly(ε-caprolactone) | $\text{+}(CH_2)_5\text{–}COO\text{+}_n$ | 213 | 336 | 19 |
| | | 205 | 330 | 20 |
| | | – | 336 | 21 |
| | | 202,213 | – | 22 |
| | | 210 | 334 | 23 |

The miscibility between these two polymers may be attributed to the presence of a specific interaction, already suggested for polylactone–PVC blends[4,17], between the carbonyl group of the polylactone and the $\alpha$-hydrogens of PVC.

## ACKNOWLEDGEMENTS

The authors thank Daniel Ouellet for X-ray, viscosity and stress–strain measurements, and Joseph Noah for dynamic mechanical measurements. They also thank the National Research Council of Canada and the Ministry of Education of the Province of Québec (FCAC program) for the research grants that supported this work.

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