CHEMISTRY LETTERS, pp. 659-662, 1973. Published by the Chemical Society of Japan

THE VISCOELASTIC CRYSTALLINE ABSORPTION OF POLYGLUTAMIC ACID ESTERS

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The viscoelastic crystalline absorption has been observed for the solid poly-γ-methyl-D-glutamate and poly-γ-benzyl-L-glutamate cast from various solvents. The temperature range of crystalline absorption (180 to 210°C) corresponds to the temperature range in which the lattice spacing deviates from linear expansion and also, the average size of crystallite increases extremely with increasing temperature.

There have been reported many investigations concerning dynamic mechanical properties of poly-γ-methyl-L-glutamate (PMLG) and poly-γ-benzyl-L-glutamate (PBLG)$^{1-4)}$. In general, two absorption mechanisms have been observed and it is concluded that the low temperature absorption (0-20°C) is attributed to the motion of side chains and the high one (100-140°C) is in relation to the segmental motion in the distorted part of main chain. In this paper, we have investigated the nature of the newly observed absorption which locates in the temperature range of 180 - 210°C using poly-γ-methyl-D-glutamate (PMDG) and PBLG from various solvents.

The solid-state films of PMDG and PBLG were cast from the solutions in the α-helix forming solvents of dichloroethane (DCE) and chloroform ($CHCl_3$) at room temperature. The x-ray photographs of these solid-state films show to be in the form of the α-helix. Also, PMDG in the form of the β-pleated sheet was obtained from solution in dichloroacetic acid (DCA) at 40°C after the aging period of 50 days. Dynamic mechanical measurement was carried out on a Rheovibron over a temperature range of 50 - 230°C at 110 Hz. Lattice spacing and the average size of crystallites were calculated from Bragg angle at the diffraction peak and the half width of the integrated intensity of $(10\bar{1}0)$ reflection, respectively.

Figure 1 shows plots of tan δ against temperature for the PMDG film cast from solution in DCE (open circles) and the same sample annealed at 215°C for 30 minutes (filled circles). Two relaxation regions are discernible in the temperature range investigated and these are labelled α and β in order of decreasing temperature. It is apparent that the α absorption peak remarkably appears and the β absorption peak corresponding to the segmental motion in the disordered part of main chain, decreases in magnitude upon annealing. The x-ray photograph of figure 1 exhibits the striking increase of degree of crystallinity upon annealing. Therefore, the α absorption may reflect manifestation of some kinds of molecular motions within the crystalline region.

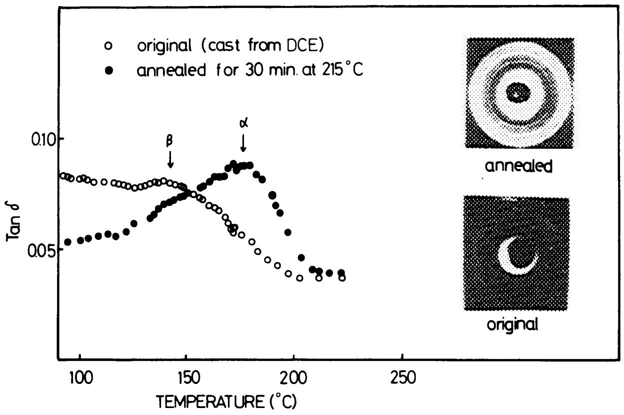

Figure 1. Temperature dependence of tan δ for original and annealed PMDG cast from solution in DCE.

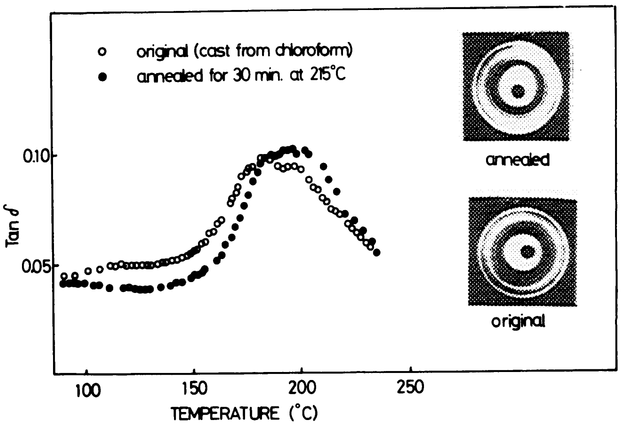

Figure 2. Temperature dependence of tan δ for original and annealed PMDG cast from solution in $CHCl_3$.

Figure 2 shows the temperature dependence of tan δ for PMDG cast from solution in $CHCl_3$ and also, annealed at 215°C for 30 minutes. The β absorption which appears as a small shoulder for the original PMDG, almost disappears and also, the peak temperature of the α absorption is raised upon annealing. The magnitude of activation energy for the α absorption was 111 kcal/mol based on the frequency dependence of temperature location of tan δ peaks. In contrast to the tan δ curve of the original PMDG prepared from DCE solution, the apparent α absorption peak has been observed without any annealing treatment in the case of the original PMDG cast from solution in $CHCl_3$. This tan δ behavior is consistent with the result that, as expected from the x-ray photograph, the degree of crystallinity for the original

PMDG solid is comparable with that for the annealed one. Though the important factor in determining the degree of crystallinity or the molecular packing within the crystalline phase has not been extensively investigated here, it may be in relation to the affinity of the α-helix forming solvents such as $CHCl_3$ and DCE for PMDG and the crystallization rate determined by the evaporation rate of solvent and temperature.

Figure 3 shows a plot of thermal expansion of lattice spacing of $(10\bar{1}0)$ which corresponds to the backbone separation of the α-helix, against temperature for PMDG cast from solution in $CHCl_3$. The lattice spacing-temperature plot exhibits a distinct break at about 145°C and then, deviates from the linear expansion around this temperature. This temperature range seems to be consistent with the temperature where the tan δ curve in the temperature range of the α absorption starts to deviate from the base line. The similar relationship between the thermal expasion of lattice spacing and the temperature range of the crystalline absorption has been previously reported in the case of high density polyethylene$^{6)}$. It is easily understood that the onset of rotational or translational motion of molecular chain within the crystalline phase may become possible due to large amplitude of molecular chain vibration activated upon heating, being accompanied by remarkable thermal expansion of lattice spacing and therefore, manifestation of these molecular motion must be in close relation to the α absorption. Also, the average size of crystallite along $<10\bar{1}0>$, $\bar{D}_{10\bar{1}0}$, evaluated from Hosemann's paracrystalline analysis$^{7)}$ exhibits remarkable increase around at 140°C. This indicates the onset of molecular rearrangement within the crystalline phase. Therefore, it has decisively been confirmed by the measurements on thermal expansion of lattice spacing and $\bar{D}_{10\bar{1}0}$ that the α absorption may be attributed to certain motion such as rearrangement of molecular chains within the crystalline phase.

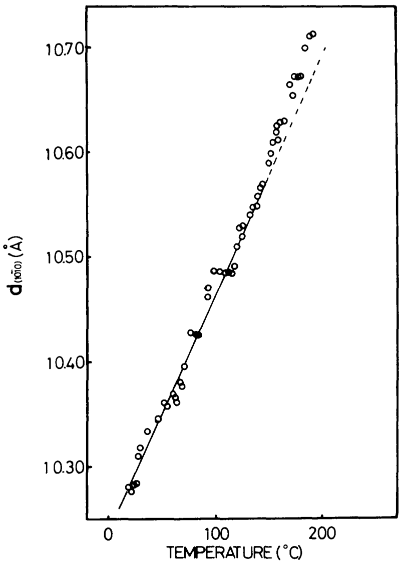

Figure 3. A plot of thermal expansion of lattice spacing against temperature for PMDG cast from solution in $CHCl_3$.

The crystalline absorption has also been observed for PBLG cast from $CHCl_3$

solution and PMDG from DCA solution (so-called random solvent) as shown in figure 4. PMDG cast from solution in DCA is in the form of the antiparallel-chain pleated sheet (β-form)[5]. The absorption peaks which locate around at 120°C for PBLG and 105°C for PMDG have been reported to arise from the segmental motion in the disordered part of the texture essentially in the α- and the β-forms[4,8], respectively. New absorption peaks observed around at 210°C for PBLG and at 180°C for PMDG are compared with the α absorption of PMDG cast from DCE and CHCl$_3$ and therefore, it seems reasonable that they reside in the crystalline absorption.

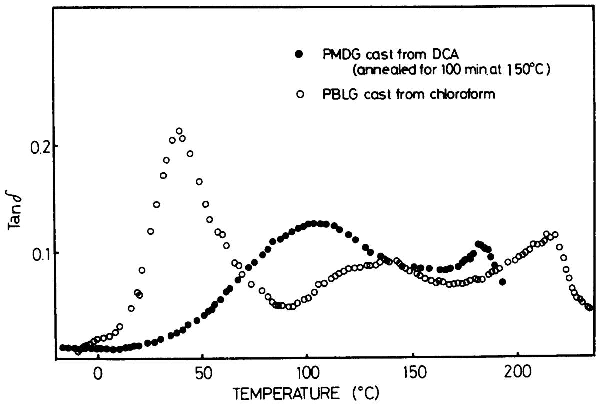

Figure 4. Temperature dependence of tan δ for PBLG cast from CHCl$_3$ solution and PMDG cast from DCA solution.

It was concluded in the dynamic mechanical measurements, x-ray studies and measurements on the thermal expansion of lattice spacing and $\bar{D}_{10\bar{1}0}$ mentioned above, that the α absorption is associated with molecular motion within the crystalline region, though it remains as future study to inquire into the mechanism of the α absorption.

We are grateful to Ajinomoto Co., Ltd. for supplying a sample of PMDG.

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(Received May 2, 1973)