CHEMISTRY LETTERS, pp. 1269-1270, 1973. Published by the Chemical Society of Japan

PRESSURE EFFECT ON β RELAXATION PROCESS IN CHLORINATED POLYETHYLENE AND POLYVINYLACETATE

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The β relaxation processes of chlorinated polyethylene vulcanizate (CPE) and polyvinylacetate (PVAc) were investigated by dielectricity in a frequency range of 30 ∿ 3×10^5 Hz, a temperature range of -50 ∿ 20 °C and a pressure range of 1 ∿ 600 Kg/cm^2. Both superpositions on temperature and pressure were possible for CPE, but not for PVAc, and the behaviors of the activation volume $\Delta V^\ddagger$ in CPE and PVAc were significantly different from each other.

It has been generally accepted that the β process is attributed to the side group motion in polymers with rotatable dipolar side groups and to the local mode motion in polymers without such side groups. Recently Goldstein presented his single hypothesis for the origin of the β process.[1,2,3] In order to clarify this point, the dielectric properties of CPE and PVAc were investigated at various temperatures, pressures and frequencies. The CPE studied here contained 39.1 wt% of chlorine, and proved to have no side group and to be amorphous by X-ray diffraction and NMR,[4] whereas the PVAc had rotatable acetyl side groups.

The complex dielectric constants $\varepsilon^*=\varepsilon'-i\varepsilon''$ under an elevated hydrostatic pressure were measured using a three electrode system in a high pressure vessel. The values of $\varepsilon' - \varepsilon_\infty$ and ε'' reduced by $\varepsilon_0 - \varepsilon_\infty$ for CPE are plotted as a function of logarithmic frequency in Fig. 1, where the values of the static dielectric constant ε_0 in the glassy state and the dielectric constant of high frequency extreme ε_∞ were evaluated from Cole-Cole plots. All frequency plots are superposable for all temperatures and pressures. The frequency plots of $\varepsilon''/\varepsilon''_{max}$ gives a master curve which is more precise than that of $\varepsilon''/(\varepsilon_0-\varepsilon_\infty)$ in CPE. In the case of PVAc, neither plots of $\varepsilon''/(\varepsilon_0-\varepsilon_\infty)$ nor $\varepsilon''/\varepsilon''_{max}$ for any temperature or pressure give a master curve, as shown in Fig. 2.

Fig. 3 shows the shift factors of the β process in CPE as a function of temperature. The activation enthalpy depends on the applied pressure, and the pressure dependence of the shift factors, i.e., the activation volume, changes with temperature as shown in Fig. 4. The apparent activation volumes of PVAc are also shown in Fig. 4. As no superposition was possible for PVAc, the apparent activation volumes were obtained from the pressure dependence of the frequency at which ε'' reached its maximum value. In this temperature range the activation volume of CPE decreases and reaches zero at about the glass transition temperature T_g (the T_g obtained by dilatometry is 256.6 K at 1 atm), whereas the apparent activation volume of PVAc hardly changes. From these experimental results, it is interesting to point out that the glass transition has some importance in the β process of CPE, which has no side groups.

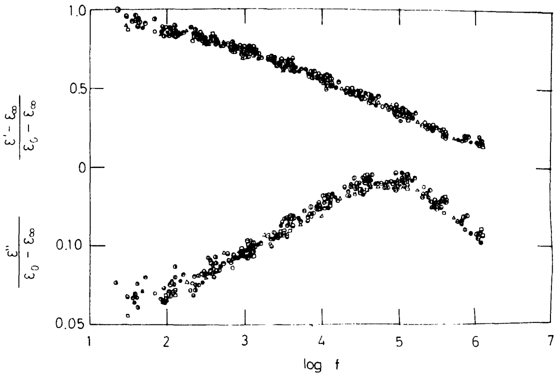

Fig. 1. Master polts for $\varepsilon' - \varepsilon_\infty$ and ε'' as a function of logarithmic frequency in CPE (the reference temperature and pressure are 232.9 K and 60 Kg/cm^2 respectively).

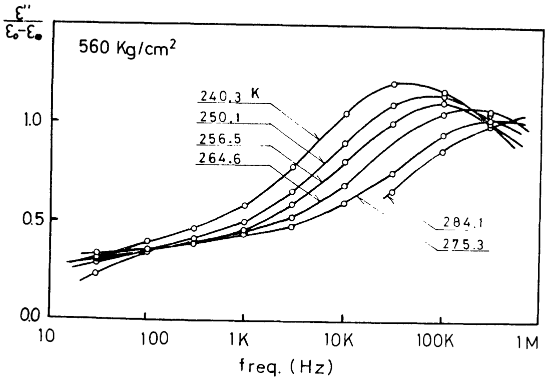

Fig. 2. $\varepsilon''/(\varepsilon_0 - \varepsilon_\infty)$ as a function of frequency in PVAc.

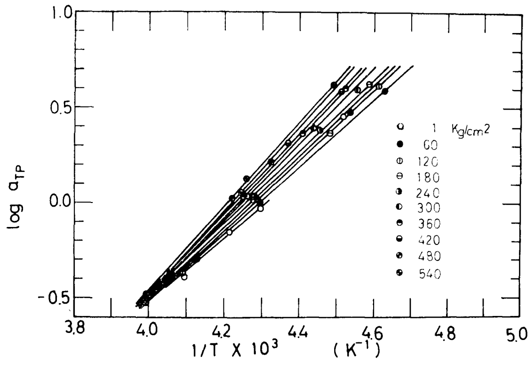

Fig. 3. Shift factor as a function of reciprocal temperature.

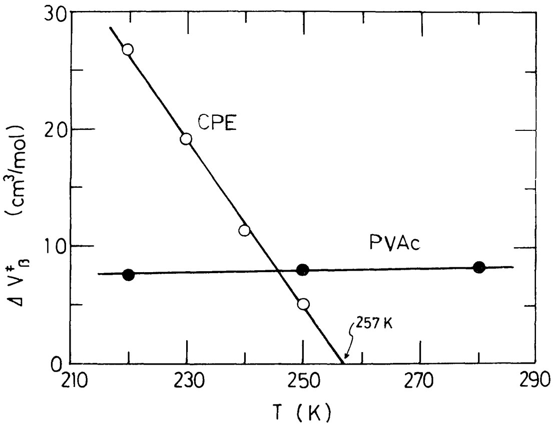

Fig. 4. Activation volume as a function of temperature.

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(Received August 25, 1973)