Chlorination of Polystyrene

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Synopsis

Chlorination of a low molecular weight polystyrene in the α position was studied by following changes in the infrared spectrum, glass transition temperature, and molecular weights of the polymer. The logarithm of the absorbance ratio at 2920 and 1500 cm^{-1} as a function of mole per cent chlorination was linear. The glass transition temperatures, determined by use of a differential scanning calorimeter (DSC), were found to obey an equation developed by Dyvik for copolymers. The molecular weight of the chlorinated polystyrene decreased as a function of chlorination.

Introduction

The glass transition temperature, $T_{g(A,B)}$, of copolymers as a function of the weight fractions of each homopolymer present has been previously investigated.[1-5] The results of these studies indicate that the $T_{g(A,B)}$ of various copolymers may have positive or negative deviations from a straight line connecting the T_g's of the respective homopolymer, display a minimum or a maximum, or be linear.[5-8]

Dyvik[9] investigated a number of copolymer systems that exhibit negative deviations from a straight line and developed an empirical equation that satisfies most of the experimental data. The equation is:

$$T_{g(A,B)} = W_{(A)}T_{g(A)} + W_{(B)}T_{g(B)} - \psi \, W_{(A)}W_{(B)} \tag{1}$$

where $T_{g(A,B)}$ is the glass transition temperature of the copolymer, $T_{g(A)}$ and $T_{g(B)}$ are the glass transition temperatures of the homopolymers. $W_{(A)}$ and $W_{(B)}$ are the weight fractions of homopolymer. ψ is an interaction parameter dependent upon the geometrical chain stiffness and intermolecular attraction and is calculated as four times the deviation of the data from a straight line connecting $T_{g(A)}$ and $T_{g(B)}$ at the 50% weight fraction composition. Recently, the equation, slightly modified, was found to fit data with a positive deviation.[5]

Oswald and Kubu[4] investigated the structural property relationships of chlorinated polyethylene and found a positive deviation of $T_{g(A,B)}$ as a function of the chlorine to carbon ratio. The increased $T_{g(A,B)}$ probably results from strong hydrogen bonding of the —H and —Cl groups between adjacent chains. In a similar manner, we have investigated the change of

infrared absorbance, glass transition temperature, and molecular weights as a function of per cent chlorination of polystyrene. The change of $T_{g(A,B)}$ with chlorination indicates loose packing of the polymer chains attributed to the addition of a bulky chlorine group to polystyrene.

EXPERIMENTAL

Chlorination of Polystyrene

Polystyrene, Dow Chemical PS-2, of low molecular weight ($\overline{M}_v \sim$ 28,000) was chlorinated at 10°C by slowly passing Cl_2 gas into a solution containing 1 mol of PS-2 dissolved in 500 ml CCl_4 and illuminated with a General Electric 400-W mercury lamp. The Cl_2 addition was held at a rate so as to maintain a slight yellow tinge to the polymer solution. Chlorine substitution was evidenced by a steady evolution of HCl gas. Samples of the polymer solution (25 ml) were periodically removed from the reaction flask, precipitated in isopropyl alcohol, dried in a vacuum oven and stored. The samples were subsequently utilized for infrared, DSC, and viscometric analysis. A correction was made for each aliquot of polymer solution removed to avoid overchlorination.

Infrared Analysis

Infrared absorbance curves were obtained on a Perkin-Elmer Model 137 double-beam spectrophotometer. The various chlorinated polystyrene samples were run at about $2M$ CCl_4 solutions in matched NaCl cells of 0.1 mm path length. The extent of chlorination of the tertiary carbon in PS-2 was followed by measuring the decrease in hydrogen absorbance at 2920 cm^{-1} as compared to the internal standard at 1500 cm^{-1} by using a baseline technique.[10] The logarithms of the absorbance ratios were then calculated and plotted as a function of Cl substitution.[11,12]

Differential Scanning Calorimeter

Thermograms of chlorinated PS-2 samples were made on a Perkin-Elmer differential scanning calorimeter, DSC-1B, at a scanning speed of 40°C/min on range of 8 mcal/sec full scale. The $T_{g(A,B)}$ of the samples were recognized as endotherms that yielded a stepwise decrease in the base line curve. Each chlorinated sample exhibited a distinct T_g.

Molecular Weight Measurements

Viscosity measurements were made at 30°C in benzene by using a Cannon-Fenske size 50 viscometer. The intrinsic viscosities were found by the usual concentration extrapolation technique and converted to a viscosity-average molecular weight $\overline{M}_v$ by use of the Ewart-Tingey relationship.[13]

$$\log \overline{M}_v = (\log [\eta] + 4.013)/0.74 \tag{2}$$

The number-average molecular weights $\overline{M}_n$ were found by use of the Mechrolab Model 301A vapor pressure osmometer.

RESULTS AND DISCUSSION

Figure 1 depicts a plot of $T_{g(A,B)}$ as a function of the weight fraction of α-chlorostyrene in polystyrene. The experimental data, represented as circles, fit quite closely to the calculated curve derived from Dyvik's equation (solid curved line). The departure of the experimental data from linearity is due principally to the substitution of the bulky chlorine atom for the α-hydrogen. This replacement produces a number of opposing effects upon the copolymer's $T_{g(A,B)}$, such as increasing the bulkiness of the polymer main chain, increasing the inter polymeric hydrogen bonding and increasing the main chain stiffness. Apparently, as depicted by our data, the net result of these opposing forces is a decrease in $T_{g(A,B)}$ caused by poor
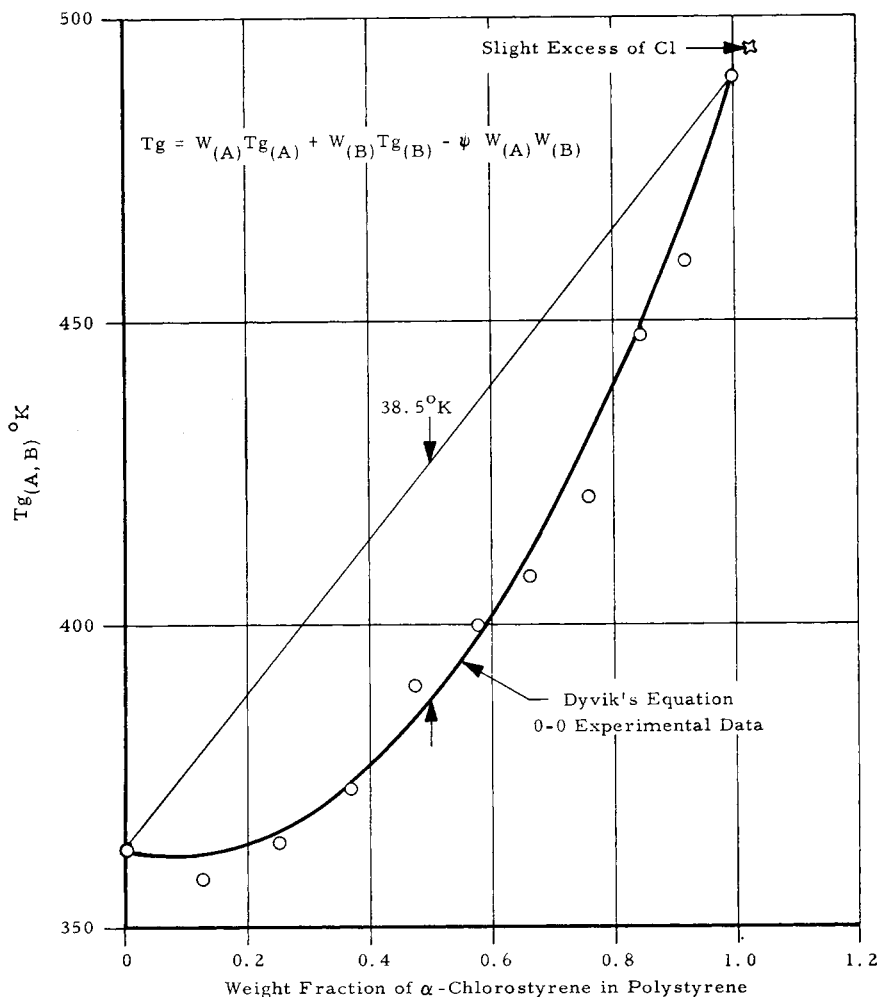

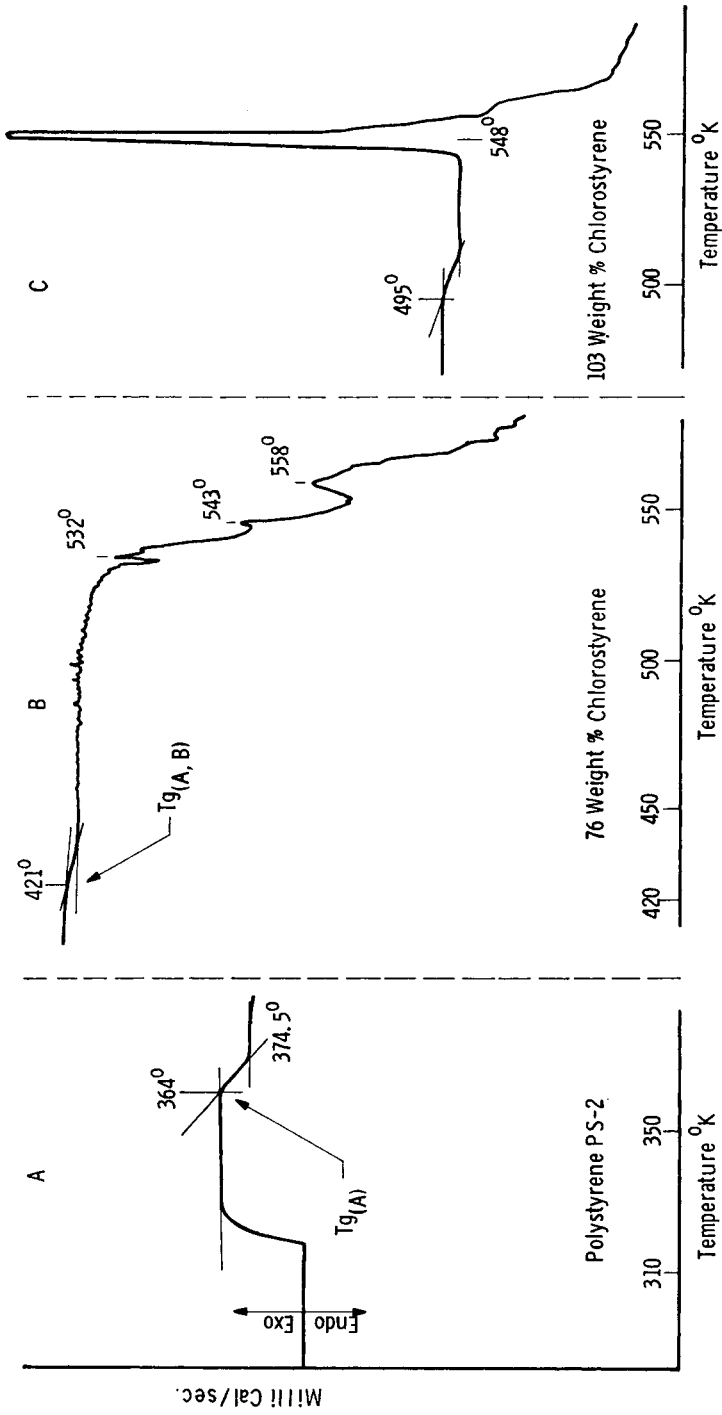Fig. 1. Glass transition temperature $T_{g(A,B)}$ as a function of chlorination.

Fig. 2. Differential scanning calorimeter data for various chlorinated polymers as a function of temperature.
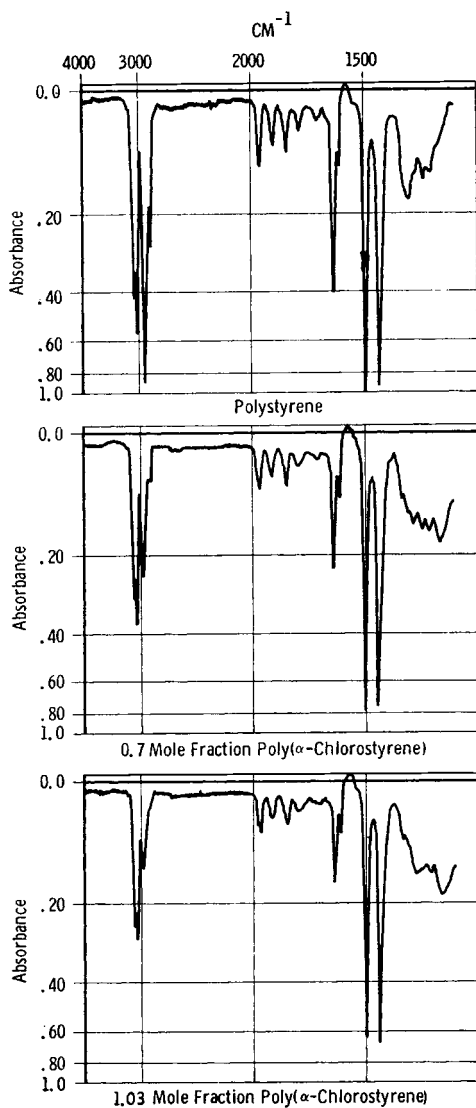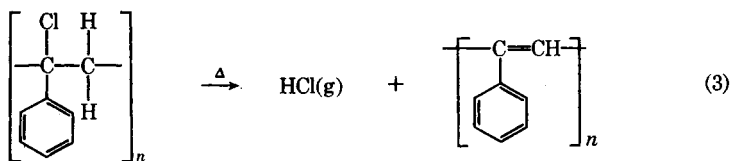
Fig. 3. Infrared absorbance curves of chlorinated polystyrene.

chain packing. Figure 2 represents thermograms of three chlorinated polystyrene samples containing 0, 76, and 103 wt-% chlorine based on hydrogen replacement. Notice the temperature advancement of $T_{g(A,B)}$ as
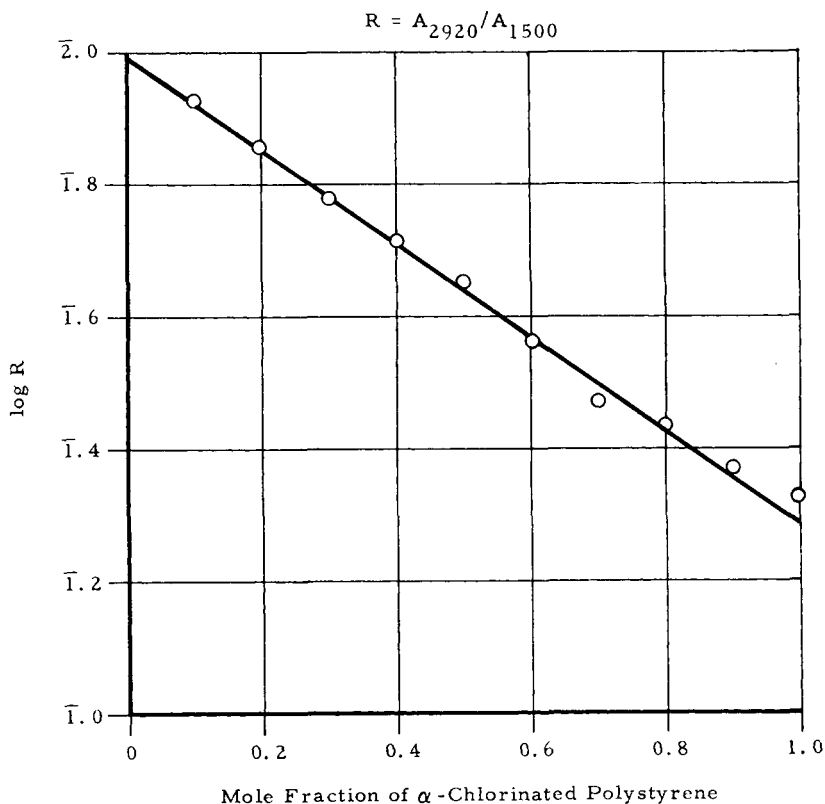
$$\left[\begin{array}{c} Cl \quad H \\ \mid \quad \mid \\ C \quad C \\ \mid \quad \mid \\ \bigcirc \quad H \end{array} \right]_n \xrightarrow{\Delta} HCl(g) \quad + \quad \left[\begin{array}{c} C=CH \\ \bigcirc \end{array} \right]_n \qquad (3)$$

$$R = A_{2920}/A_{1500}$$

Fig. 4. Logarithm of the absorbance ratio of 2920 and 1500 cm^{-1} as a function of chlorination.

the polystyrene is progressively chlorinated; in addition, distinct exothermic peaks appear resulting from the dehydrohalogenation step [eq. (3)]. The resulting polymer, polyphenylacetylene, has a number of interesting thermal and electrical properties.[14] The three exothermic peaks shown in Figure 2B result from the sensitivity of the dehydrochlorination process to neighboring groups, i.e., retardation by neighboring allylic groups.[15]

Figure 3 depicts representative infrared spectra of the copolymer as it was progressively chlorinated; Figure 4 is a plot of the logarithms of the absorbance ratio of 2920 and 1500 cm^{-1} as a function of the mole fraction of α-chlorostyrene in polystyrene. The disappearance of the absorption bands at 2920, 2850, and 1370 cm^{-1} is indicative of chlorine substitution of hydrogen at the α-position. The methylenic band at 1450 cm^{-1} did not change during chlorination thereby indicating that chlorine substitution did not occur in this position; in addition, no disubstitution of the phenyl group was observed. The internal standard used in this determination was the phenyl absorption at about 1500 cm^{-1}. This absorption band is dependent upon polymer concentration and therefore shows some fluxuation due to
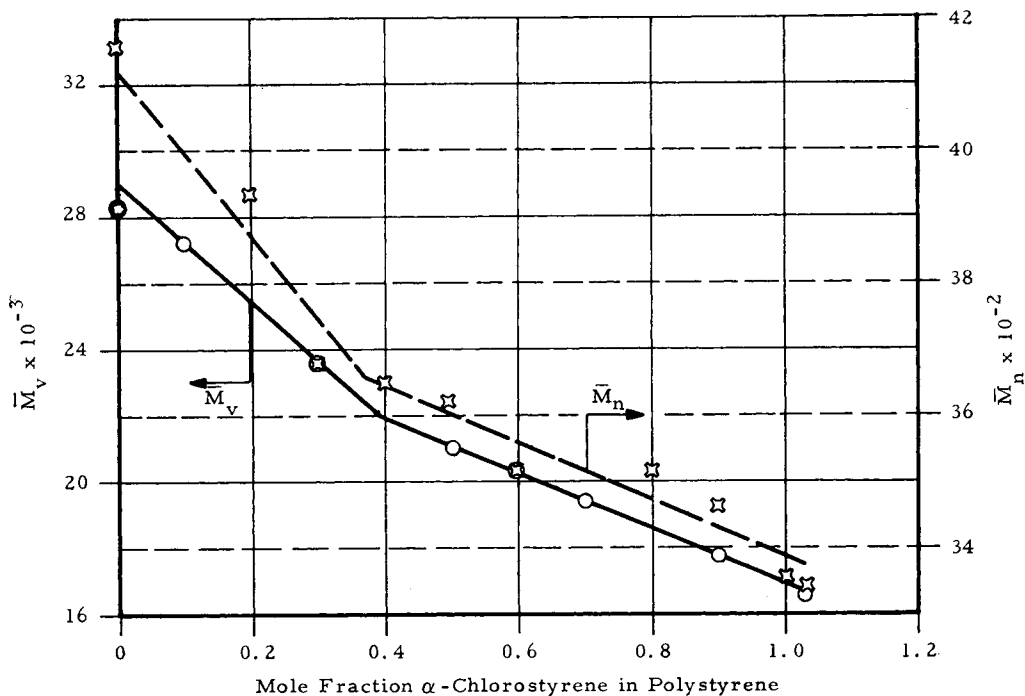
Fig. 5. Molecular weight data as a function of chlorination of polystyrene.

inexact solutions preparation.   Thus, it is apparent that the chlorination of polystyrene is an orderly process when conducted at low temperatures and low rates of chlorine addition and does preferentially substitute at the α hydrogen position.   It is also significant that by closely monitoring the infrared spectra of the polystyrene sample being chlorinated one may rapidly determine the extent of chlorination.

The viscosity-average molecular weights $\overline{M}_v$ of the various chlorinated PS fractions were calculated by using the Ewart-Tingey relationship[13] [eq. (2)] derived for polystyrene in benzene at 30°C.   The use of this equation is somewhat arbitrary as the K and a factors in the general equation $[\eta] = K\overline{M}_v{}^a$ probably do not remain constant during chlorination due to copolymer formation.   The change, however, is quite small as evidenced by the approximately constant ratio of $\overline{M}_v$ to $\overline{M}_n$ as seen in Figure 5.   This ratio is approximately 6.0.   This large value is due to the polydispersity of the original PS-2 and subsequently the chlorinated polymer.   As seen from Figure 5, the chlorination of polystyrene produces a continuous scissioning of the main chain which is proportional to the degree of chlorine substitution above and below 0.4 mol fraction of α-chlorostyrene.   At about 0.4 mol fraction of α-chlorostyrene a scissioning rate change occurs whose mechanism is not apparent.   Ultraviolet irradiation did not contribute to the scissioning process as no change in viscosity of a control sample was observed after irradiation for 5 hr at 10°C without chlorine present.

CONCLUSIONS

The chlorination of polystyrene in a CCl_4 solution at 10°C with ultraviolet radiation is an orderly process with the chlorine substituting at the α hydrogen position. During the chlorination reaction, main-chain scissioning occurs, the rate of which appears to be related to the degree of chlorine substitution. The $T_{g(A,B)}$ of the various fractions of the chlorinated polymer obeyed an empirical relationship developed by Dyvik for copolymers.

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