Aggregation of Poly(vinyl Chloride) Fractions

INTRODUCTION

Gel permeation chromatographic studies[1] indicated that the aggregation of poly(vinyl chloride) (PVC) molecules increases with molecular weight. Since the PVC materials were synthesized at the same temperature (−25°C) and yielded the same fraction of crystallinity (~15%) by x-ray diffraction following annealing, it was inferred that changes in aggregation occurred at constant stereoregularity. Further experimental evidence is reported confirming that the PVC fractions are of the same tacticity. Moreover, an increase in calorimetric glass transition temperature with increasing molecular weight is reported.

EXPERIMENTAL DETAILS

The synthesis, fractionation, and characterization of PVC materials was previously described.[1] Infrared measurements of the absorbance ratio of the bands at 635 and 693 cm^{-1} were carried out on a Beckmann IR-12 spectrophotometer at a scan rate of 20 cm^{-1}/min. Film samples approximating 0.5 to 1.0 mil thickness were cast on a KBr pellet from a 5% solution of PVC in tetrahydrofuran (THF). The THF was subsequently evaporated in a vacuum oven at 60°C for three days, after which infrared spectra did not indicate any absorption due to THF. Thermal analysis involved a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of 20°C/min. The calorimeter had been calibrated for temperature and heat of fusion with indium. A sharp discontinuity in calorimetric heating curves was identified with the glass transition temperature (T_g). The value of T_g was selected as the midpoint of the endothermal shift.

RESULTS

Values of the weight-average molecular weight ($\bar{M}_w$), the ratio of weight- and number-average molecular weights ($\bar{M}_w/\bar{M}_n$), and the weight fraction aggregate, all derived from gel permeation chromatography, and the calorimetric glass transition temperature (T_g) and the infrared (IR) absorbance ratio are listed in Table I.

DISCUSSION

The ratio of the optical densities at 635 and 693 cm^{-1} has been shown to vary with the syndiotacticity and/or crystallinity.[2-4] X-Ray diffraction studies[1] indicated that the PVC samples were noncrystalline when isolated from eluent solutions from gel permeation chromatography but could be crystallized to about 15% on annealing at 150°C. An IR ratio approximating 2.2 indicates a PVC material of about 56% syndiotacticity.[3] This ratio is, within experimental error, independent of molecular weight, demonstrating that the fractions are of the same tacticity or crystallinity. Lebedev et al.[5] have shown that the IR ratio is not sensitive to molecular weight per se for molecular weights exceeding 2000. The degree of syndiotacticity is

TABLE I
Properties of PVC Fractions

$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Aggregate fraction, %	T_g, °C	IR Ratio
18,000	1.32	2.0	95	2.29
48,700	1.26	7.7	99.5	2.11
94,200	1.23	28.2	100.5	2.24
216,000	1.61	37.7	100.5	2.28

TABLE II
Glass Transition Temperature (T_g) of PVC

$\bar{M}_w$	$T_{g(\text{observed})}$, °C	$T_{g(\text{calculated})}$, °C
18,100	95	91
48,700	99.5	97
94,200	100.5	98.5
216,000	100.5	99.5

lower than one would expect for a polymerization temperature of −25°C.[6] This may be the result of unusual initiation.[1]

It has been reported that the glass transition temperature (T_g) of PVC depends on the degree of syndiotacticity.[7,8,9] For these fractions, the variation of T_g may be simply interpreted as a dependence on molecular weight.[10] The observed variation is smaller than predicted on this basis, however. Assuming that the value of T_g in the limit of infinite molecular weight ($T_{g\infty}$) is equal to 100.5°C (Table I), values of T_g may be calculated from the following equation[10]:

$$T_g = T_{g\infty} - \frac{170{,}000}{\text{molecular weight}}.$$

Calculated values of T_g are compared to observed data in Table II. Since aggregation markedly increases the "effective" molecular weight, it is likely that the sensitivity of T_g to molecular weight is reduced.

CONCLUSIONS

Molecular weight fractions of PVC that possess the same tacticity by infrared analysis vary in aggregate content and calorimetric glass transition temperature (T_g). The T_g equals 95°C at a molecular weight of 18,100, varies by only 1°C from 48,700 to 216,000, and is 100.5°C for the latter fraction. It is suggested that molecular aggregation reduces the dependence of T_g on molecular weight.

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