Darzen's Glycidic Ester Condensation Reaction on Poly(N-Vinyl Pyrrolidone)

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SYNOPSIS

About 38% conversion of carbonyl groups into epoxy functions in the molecular chain of poly (N-vinyl pyrrolidone) using chloracetamide results in the decreased viscosity of the product. De-epoxidation of the epoxy groups introduced shows the most contributing factor towards decreased viscosity is epoxy function.

In a previous study, we reported on the synthesis of some methyl aryloxymethacrylates, the polymers we obtained by different methods, and some characterization studies, such as an evaluation of Mark–Houwink's constants, X-ray diffraction patterns of fibers, etc., performed on these polymers.[1] The present work shows the possibility of carrying out Darzen's glycidic ester condensation reaction across a polymeric carbonyl group. The use of Darzen's condensation reaction in the conversion of aldehydic and ketonic functions into epoxy function is well established in both aromatic and aliphatic compounds, including terpene ketones, by employing a host of condensing agents and a variety of condensing molecules.[2-6] No reference in the literature is found, however, for the conversion of a polymeric carbonyl into an epoxy derivative. Also, polymers or copolymers having an epoxy linkage are made from monomers containing an epoxy group, which, in turn, is introduced into the precursor through Darzen's condensation, epichlorohydrin reaction, etc. It is, however, observed that commercial poly (N-vinyl pyrrolidone), PVP, can undergo Darzen's glycidic ester condensation reaction under certain conditions. PVP finds extensive applications, especially as a water soluble polymer, and its condensation product from Darzen's reaction, which is soluble in water, is found to have a lower viscosity than PVP. In as much as viscosity reducers have

significant applications in the manufacture of adhesives, in the coating and sizing of paper and textiles, and in the conditioning of phosphates and oil drilling muds,[7] a simple method of converting PVP into a sample of low viscosity is reported.

Attempts to condense a commercial sample of poly(N-vinyl pyrrolidone), ($\overline{Mn}$ = 14,000), with ethyl chloroacetate, sodium or potassium ethoxide in ethanol, ethyl chloroacetate and potassium tertiary butoxide in t-butanol or sodamide and ethyl chloroacetate, all were unsuccessful. However, the condensation of chloracetamide with PVP, in the presence of sodium ethoxide in dry ethanol, is found to yield the epoxy-containing derivative, poly(N-vinyl 2-glycidylamido pyrrolidone), (PVGP). Under the conditions used, the reaction never proceeded at all in the former cases. The epoxy group introduced in PVP, using chloracetamide as precursor, is found to lower the viscosity of the polymer considerably, as shown by the increase in viscosity of the derivative when a de-epoxidation reaction was conducted with hydrobromic acid at different temperatures. The variation of viscosity of both PVP and PVGP with temperature has also been studied.

EXPERIMENTAL

Sodium ethoxide (5 g of pure sodium to 200 mL of dry and distilled ethanol) was added over a period of 2 h with constant rapid stirring to a 1 : 1 w/w ratio mixture of PVP (25 g) and chloracetamide (25 g). The mixture kept at 283 K.

Keeping the temperature constant, stirring was continued for another $1\frac{1}{2}$ h and then the alcohol was distilled off under reduced pressure in a steambath. The residual solution was precipitated in methanol and dried. We observed that the condensation did not proceed at lower temperatures. A blank experiment was also carried out with PVP under identical conditions.

The IR spectrum of the Darzen's condensation product was taken on a KBr pellet using a Perkin-Elmer IR Spectro–photometer. Molecular weights were determined from the intrinsic viscosity values using Mark–Houwink's constants for PVP. Viscosity measurements, including those with HBr (0.001 N) were made in a Cannon–Fenske viscometer on the aqueous solutions of both polymers. Percent Darzen's condensation was determined argentimetrically. All the chemicals used were of "AnalaR" grade and the PVP used was a commercial sample of SD's Fine Chemicals Laboratories, India.

RESULTS AND DISCUSSION

The condensation product (PVGP) was purified by dissolving in water and precipitating in dry methanol three times. Molecular weights of PVP in the blank experiment, and PVGP determined viscometrically using K and α values for PVP at 20°C (K = 64 and α = 0.58),[8] show that the former had almost the same value (13,200) and the latter was 5.85 $\times$ 10^3.

The suggested molecular disruption of PVP in sodium ethoxide at 283 K is unexpected, as PVP has been reported to be highly stable and becomes permanently insolubilized when heated in air to 150°C or heated in strong alkali at 100°C. The viscosity of PVP is also reported to remain unchanged over the pH range of 1–10, although it is observed to increase with concentrated hydrochloric acid.[9] The K and α values might differ for PVGP and so the reported molecular weight of PVGP should not be taken as accurate.

The chloride ion, released in the condensation of the acetamide group to the carbonyl function, was estimated argentimetrically with potassium chromate indicator and this value was used to determine the percentage of condensation of chloracetamide to PVP; the percentage of condensation was calculated to be 37.5.

The infrared spectral values with prominent absorption peaks at 2990–3050 cm^{-1}, 1240–1280 cm^{-1}, 930 cm^{-1}, and 770 cm^{-1}, confirm the presence of the epoxy linkage. So, the condensation reaction is represented as
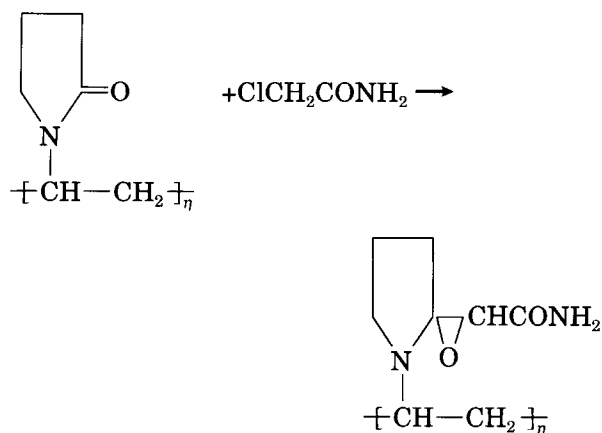
Almost identical trends were observed in the decrease of the [η] values of PVP and PVGP (Table I, Figure 1) with increasing temperature, which contrasts with the systems of polystyrene in decalin[10] and styrene-p-chloro styrene,[11] where the rise in [η] values, with increasing temperature, was reported to be due to conformational changes with the expansion of the chain favoring polymer–solvent contacts.[10,11]

The contributors for the steep fall in viscosity in PVGP are:

1. The molecular mass of PVGP (calculated using the K and α values of PVP), which is found to be almost half the molecular mass of PVP (5.85 $\times$ 10^3 and 13.20 $\times$ 10^3, respectively),
2. The epoxy linkage in PVGP.

The evidence for the second contributing factor is obtained by the removal of the epoxy linkage in PVGP. The epoxy linkage is converted into bromohydrin when treated with hydrobromic acid. A 0.001 N HBr solution was slowly added to 2% aqueous solutions of PVGP and viscosity measurements were carried out at 298 K, 308 K, and at 318 K. Ten percent solutions of both PVP and PVGP absorb at 210 nm. Relative viscosities determined

Table I Changes of [η] with Temperature for PVP and PVGP

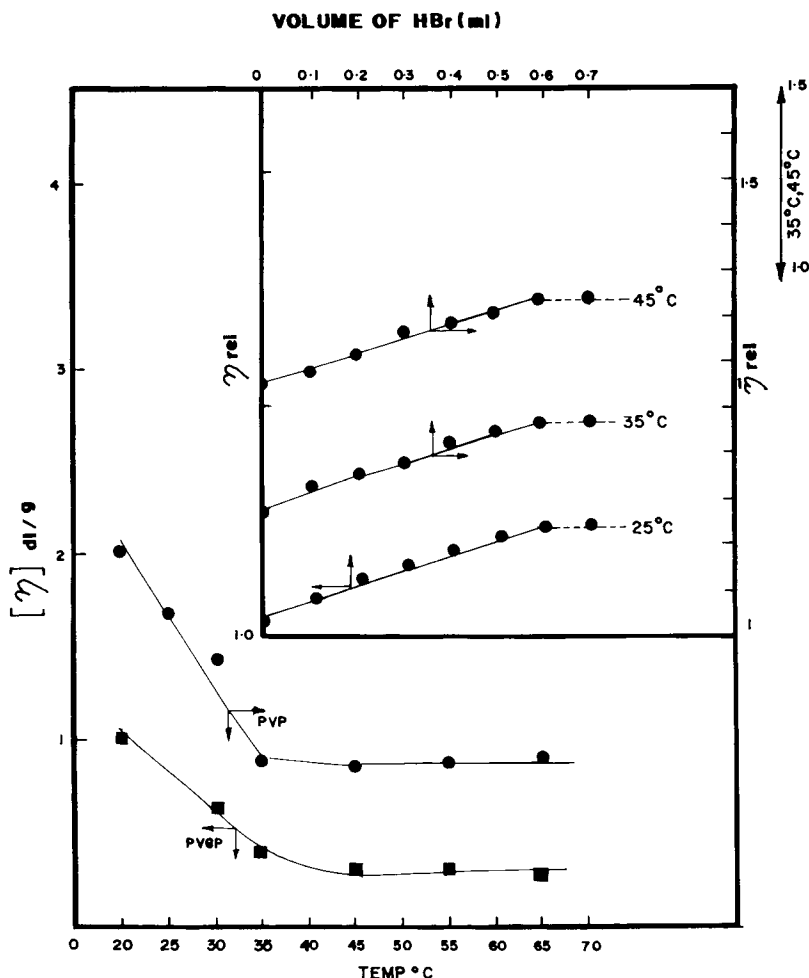| Temperature (K)	[η] PVP (dl/g)	[η] PVGP (dl/g)
293	3.08	0.98
298	2.35	—
303	1.85	0.71
308	0.75	0.42
318	0.70	0.28
328	0.76	0.30
338	0.82	0.18

Figure 1   [η] vs. temperature for PVP and PVGP.

for these solutions were found to increase steadily with increasing volume of HBr till a limiting value at each temperature, as shown in the figure, was reached. These values at the different temperatures are:

1. 1.229 at 25°C,
2. 1.261 at 35°C,
3. 1.228 at 45°C.

The contribution by epoxy linkage towards the total lowering of viscosity of PVP was established by using these values in the calculation of percentage contribution, which is calculated to be nearly 20.

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