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ENTHALPY OF MALEIC ANHYDRIDE POLYMERIZATION IN THE PRESENCE OF POLY-4-VINYLPYRIDINE

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ABSTRACT

The polymerization of maleic anhydride in the presence of poly-4-vinylpyridine was studied by means of differential scanning calorimetry with isothermal and dynamic tests. The absolute ΔH value increases with the percentage of the base. The enthalpy of the polymerization reaction of maleic anhydride in the presence of a large excess of poly-4-vinylpyridine (-85.5 kJ per mol maleic anhydride) was obtained by extrapolation from measurement performed in dimethyl sulphoxide solutions.

INTRODUCTION

In a previous work [1] the anionic polymerization of maleic anhydride in the presence of pyridine was studied using differential scanning calorimetry. For this reaction the ΔH value obtained by extrapolating the molar ratio between maleic anhydride and pyridine to zero monomer concentration is -93.6 per mol maleic anhydride.

The aim of this investigation was to study the polymerization reaction of maleic anhydride in the presence of a polymer of 4-vinylpyridine.

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EXPERIMENTAL

Materials

Maleic anhydride (MA), > 99% purity and dimethyl sulphoxide-d_6 > 99.95% atom D were obtained from Fluka.

Poly-4-vinylpyridine (poly(4-VPy)) was obtained by anionic polymerization with butyl lithium as initiator [2]. The polymer has the following characteristics: %N = 13.06, $[\eta]$ measured in methanol at 25 °C = 0.235 dl g^{-1} and $\overline{M}_v = 21600$ on the basis of the relation [3]

$$[\eta]^{25}_{\mathrm{MeOH}} = 2.4 \times 10^{-4} \overline{M}_v^{0.69}$$

The glass transition temperature, measured by means of DSC, is 375 K.

Procedure

DSC curves were obtained on a Perkin–Elmer DSC-2 instrument equipped with a Perkin–Elmer Thermal Analysis Data Station 3600. Samples of 0.5–3.5 mg MA and poly(4-VPy) were weighed in aluminium pans. The pans were hermetically sealed with covers. Some experiments were performed in dimethyl sulphoxide (DMSO) solution: the molar concentration of MA was in the range 3–3.5. The instrument was preset at 303 K and the sample was either heated to 453 K at 5 K min^{-1} (dynamic test), or rapidly heated (320 K min^{-1}) to 323 K (isothermal test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output.

The course of the reaction in deuterated DMSO solution at 299 K was estimated using NMR spectroscopy directly on the solution in the NMR tube. ^1H NMR spectra were recorded on a Varian XL 200 FT instrument.

RESULTS

Preliminary measurements have demonstrated that MA reacts in the presence of poly(4-VPy) producing polymers.

Figure 1 shows the MA conversion at 299 K versus reaction time when performing the reaction directly in an NMR tube and employing a deuterated DMSO solution of the mixture. The molar concentration of MA is 0.4 and the molar ratio R is 1.08. The progress of the reaction was followed by measuring the change with time of the integral of the signals from the maleic protons divided by the integral of the signals from the four protons of the pyridine unit.

Figure 2 shows the change in the reaction enthalpy with the molar ratio $R = [\mathrm{MA}]/[\mathrm{poly(4\text{-}VPy)}]$ in isothermal tests at 323 K in the absence of a solvent. Preliminary measurements have indicated that the reaction does not

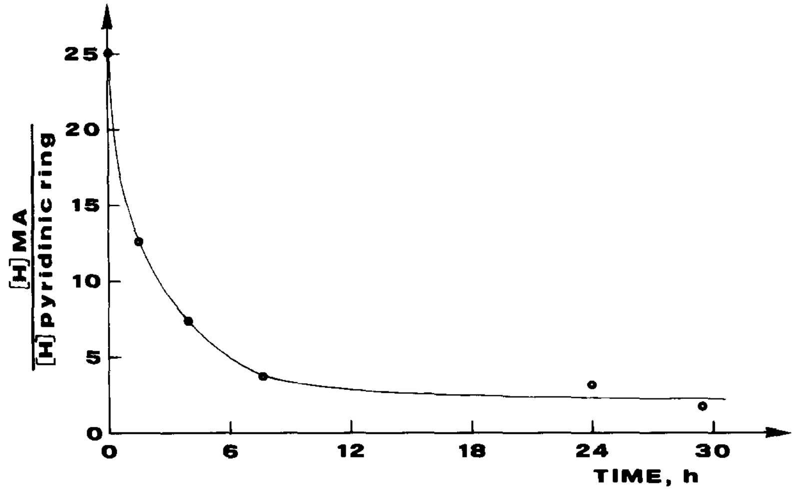

Fig. 1. Change in the ratio [H]MA/[H]pyridinic ring at 299 K with time for $R = [MA]/[poly(4\text{-}VPy)] = 1.08$.

occur in a meaningful way below this temperature; at higher temperatures it proceeds at too a high a rate to allow measurements to be made.

Irreproducible results were obtained in dynamic tests in the absence of a solvent.

The best results were obtained in dynamic tests with solutions of the reactants in DMSO. Figure 3 shows how the reaction heat increases with the

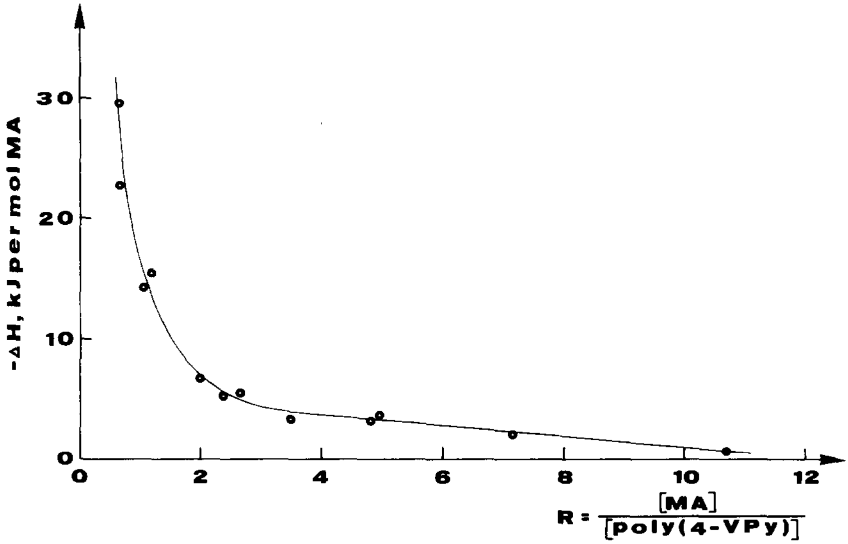

Fig. 2. Change in the reaction enthalpy in the absence of a solvent with molar ratio $R = [MA]/[poly(4\text{-}VPy)]$. Reaction temperature, 323 K.

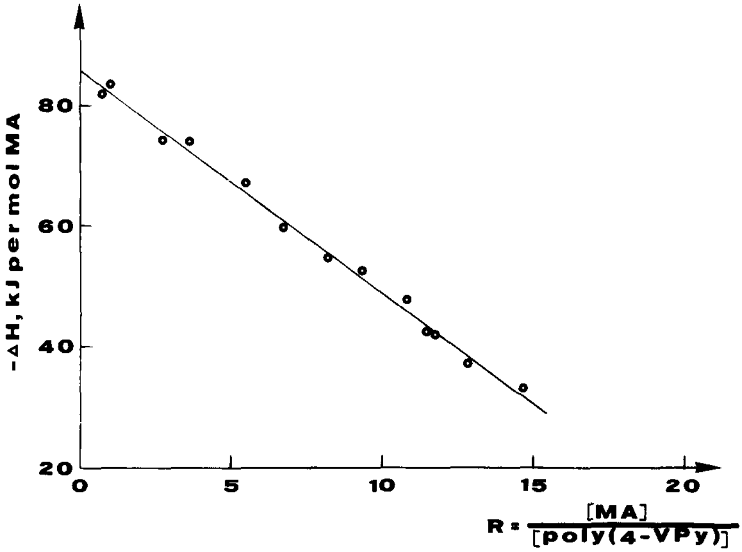

Fig. 3. Change in the reaction enthalpy in the presence of DMSO with molar ratio $R = [\text{MA}]/[\text{poly(4-VPy)}]$. Scanning rate, 5 K min^{-1}.

reduction of the molar ratio $R = [\text{MA}]/[\text{poly(4-VPy)}]$. The study was carried out in the temperature range 303–453 K with molar ratios in the range 0.7–14.7. The points fall satisfactorily on a straight line which, by extrapolation to zero MA concentration, gives a ΔH value of -85.5 kJ per mol MA for this reaction. Figure 4 shows a typical dynamic DSC curve of a MA–poly(4-VPy) mixture in DMSO with a molar ratio $R = 0.98$.

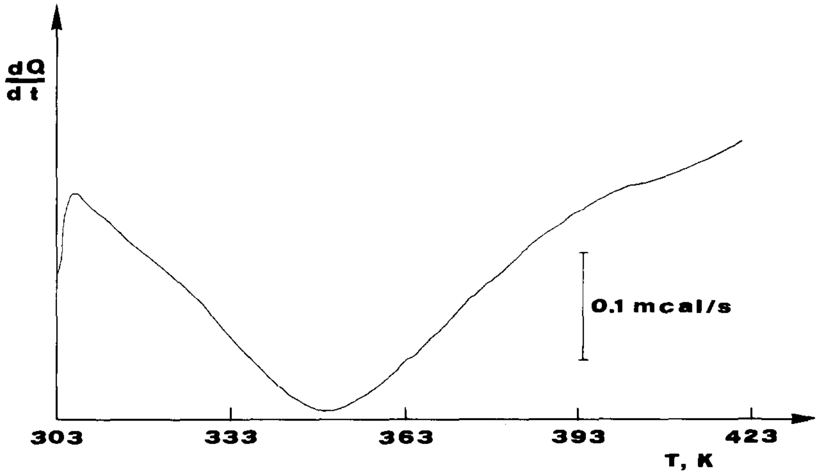

Fig. 4. Typical dynamic DSC curve of a MA–poly(4-VPy) mixture in DMSO with $R = [\text{MA}]/[\text{poly(4-VPy)}] = 0.98$. Scanning rate, 5 K min^{-1}.

DISCUSSION

Figure 2 illustrates the low reactivity of the system without a solvent, at least up to a molar ratio of 2 which corresponds to a mixture containing about 33% by weight of poly(4-VPy). At lower molar ratios, the reaction proceeds with a strong increase in the heat evolved. The values so obtained do not allow a reliable extrapolation of the curve. These results probably reflect the restriction imposed on the activity of the basic groups by the macromolecular structure. This hypothesis is strengthened by examination of Fig. 5 in which the curves obtained by studying the reaction of MA with poly(4-VPy) and with pyridine [1] are compared. This figure clearly indicates the higher reactivity of pyridine which is due to a higher molecular mobility, as both reactants have comparable p*K* values on the basis of a comparison of substituted pyridines [4]. Furthermore the MA–pyridine system can be considered homogeneous at 328 K, whereas, in the other system, the molten MA is in the presence of poly(4-VPy) which is still in the solid state.

The MA–poly(4-VPy) system begins to react from high molar ratios if solutions of the polymer in DMSO are used. Figure 3 shows that the absolute ΔH value increases with the amount of poly(4-VPy) and the straight line obtained can be extrapolated to give the reaction enthalpy of MA in the presence of a large excess of base. The value obtained, −85.5 kJ per mol MA, is very close to that found when pyridine is used (−93.6 kJ per mol MA).

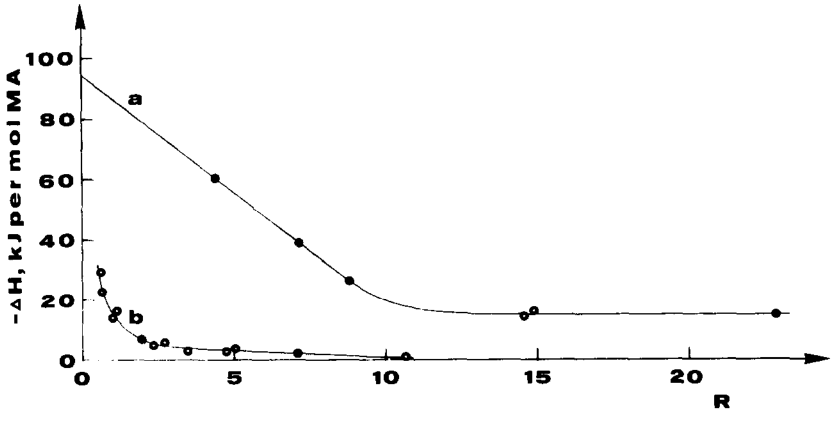

Fig. 5. Change in the reaction enthalpy with molar ratio R. Curve a, $R = [\mathrm{MA}]/[\mathrm{Pyridine}]$ and reaction temperature = 328 K. Curve b, $R = [\mathrm{MA}]/[\mathrm{poly(4\text{-}VPy)}]$ and reaction temperature = 323 K.

CONCLUSIONS

The ΔH value of -85.5 kJ per mol MA, obtained by extrapolation, is probably a result of the sum of the ΔH values for the polymerization reaction and the reactions of chain interruption. If this reaction also occurs with formation of a complex MA–poly(4-VPy), a ΔH value reflecting the formation of this starting complex should be considered. A real graft co-polymer can be generated from the complex at the end of the process.

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