

THERMAL STABILITY OF POLYMER-SUPPORTED BORONIC ACIDS FUNCTIONALIZED WITH MOLYBDENUM DERIVATIVES

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(Received in final revised form June 14, 1988)

ABSTRACT

Two novel molybdenum-containing dihydroxyboryl-substituted resins (used as catalysts for oxygen-transfer reactions) have been prepared and thermally analyzed. Simultaneous TG-DTA experiments were run to assess the effect of the grafting procedure on their thermal behaviour. Additional information concerning the structural modifications observed was obtained by infrared spectroscopy.

INTRODUCTION

Previous studies of the thermal stability of polymers in the presence of transition metal ions have been directed to evaluation of the influence of inorganic pigments or polymerization catalyst residues [1]. In the case of transition metal catalysts supported on a polymer matrix, thermal stability is a strict requirement only when a regeneration step is introduced in the catalyst cycle. This was the case for the supported Mo⁶⁺ used in the liquid-phase epoxidation of olefins [2,3]. Mo⁶⁺ has been grafted to polymeric resins using a boronic group as a bridge between the metal ion and an aromatic ring of the

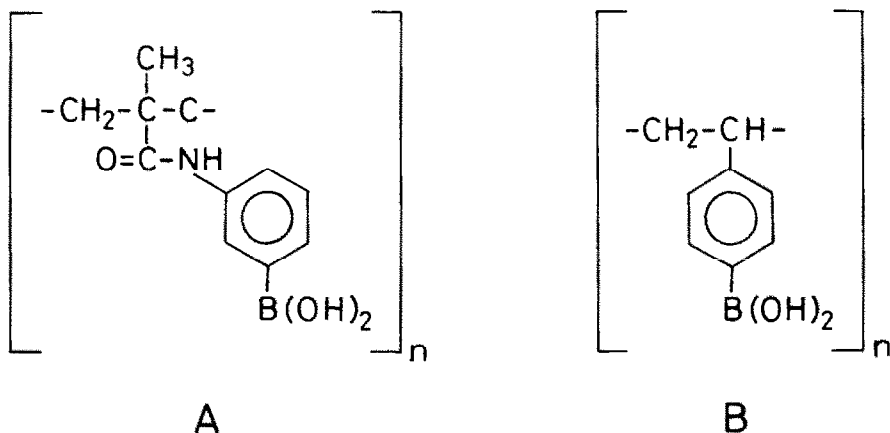


Fig. 1. Dihydroxyboryl-substituted resins investigated.

polymer.

Immobilized boronic acids are marketed for use as protecting groups in organic synthesis [4] and chromatographic phases in many separations of biological interest [5]. Thermal stability of the immobilized boronic acids and the way in which molybdenum grafting affects the degradation of their support are discussed in this paper.

EXPERIMENTAL

Simultaneous TG-DTA runs were carried out on a Mettler TA2000C thermoanalyzer. Specimens of 5 mg were heated at a rate of 20 °C min⁻¹ under gas flow (nitrogen or air). Platinum crucibles with a pierced lid were used.

Specimens heated to intermediate temperatures were analyzed by IR spectroscopy in KBr pellets.

Two different polymer matrixes were examined (Fig. 1). Support A was a commercially available resin (Boric acid gel Ega-Chemie) obtained by cross-linking copolymerization of dihydroxyborylanilino-substituted metacrylic acid with 1,4-butanediol dimetacrylate [6]. The boron content was 1.4% on a dry base. Support B was a solvent-swelling 1% divinylbenzene-styrene copolymer functionalized with boronic acid groups by using a multi-steps process according to Farrall [7]. The boron content was 2.7% by weight. Both resins were functionalized with Mo⁶⁺ by salification with H₂MoO₄ in an acid medium at pH 1. Acid-base interaction accompanied by water elimination allowed the grafting of one molybdate ion per boronic group [3,8].

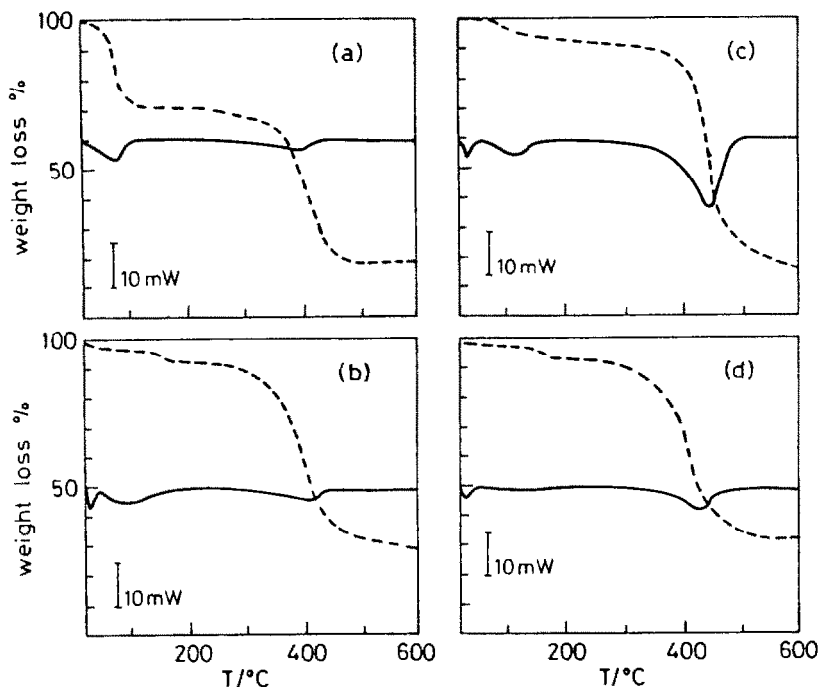


Fig. 2. TG (---) and DTA (—) traces under N_2 flow: (a) resin A, (b) Mo-grafted resin A, (c) resin B, (d) Mo-grafted resin B.

RESULTS AND DISCUSSION

The results of the TG-DTA tests in inert atmosphere are set out in Fig. 2. The auxiliary spectroscopic findings indicate that some of the phenomena observed in Fig. 2 can be attributed to modifications of the inorganic functions. Accordingly, starting from either A and B, the presence of boronic end groups is confirmed, since strong absorption near 1340-50 (broad) and 3450 (broad) cm^{-1} (Figs. 3 a and 4 a) due to B-O and OH stretching vibration respectively is observed. Indeed, similar assignments have already been made for many boron-substituted aromatic compounds containing B-O bonds [9].

Starting from unsupported A or B and up to 300 °C, the thermal process was tentatively monitored by following the decrease in intensity of the OH stretching vibration. Two definite results were obtained; even under very strictly controlled experimental conditions, it is very difficult to evaluate the quantity of water definitely removed from the B-OH functional groups. At temperatures higher than 300 °C, when thermal degradation becomes evident, by collecting samples in their early stages, it can be shown that a major shift of

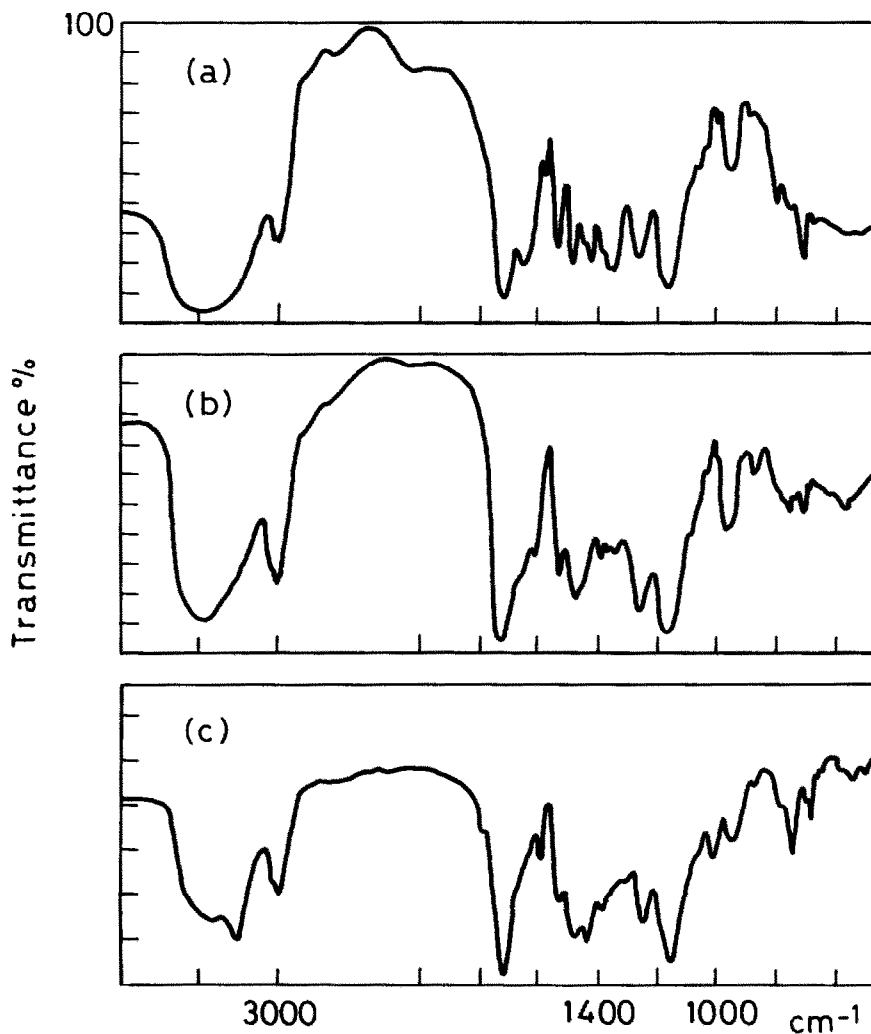
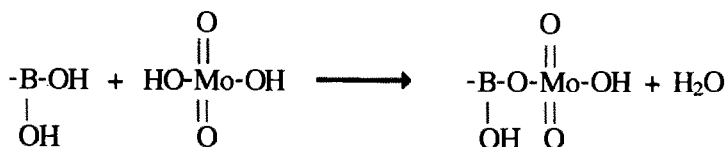


Fig. 3. IR spectra of resin A: (a) as such, (b) Mo-grafted, (c) treated at 300 °C under N₂.

the B-O stretching mode occurs to higher frequencies (Figs. 3 c and 4 c). This shift is clearly reminiscent of the modification of the B-O stretching observed [3] when passing from the B-OH (acid) to the corresponding B-O-Mo group (Figs. 3 b and 4 b):



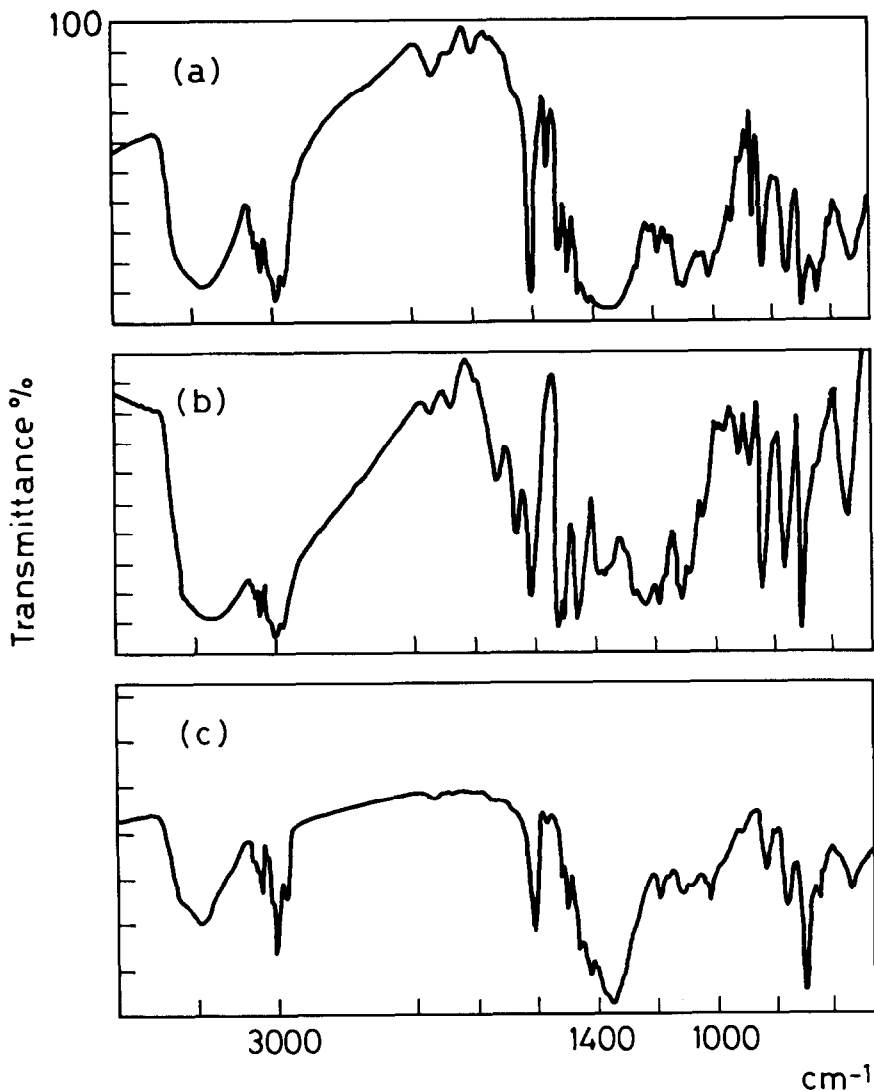
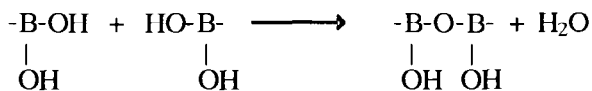


Fig. 4. IR spectra of resin A: (a) as such, (b) Mo-grafted, (c) treated at 300 °C under N₂.

Accordingly, the major modification occurring beyond 300 °C may be assumed to involve evolution of the B-OH (acid) group to the corresponding B-O-B (anhydride) group of the type:



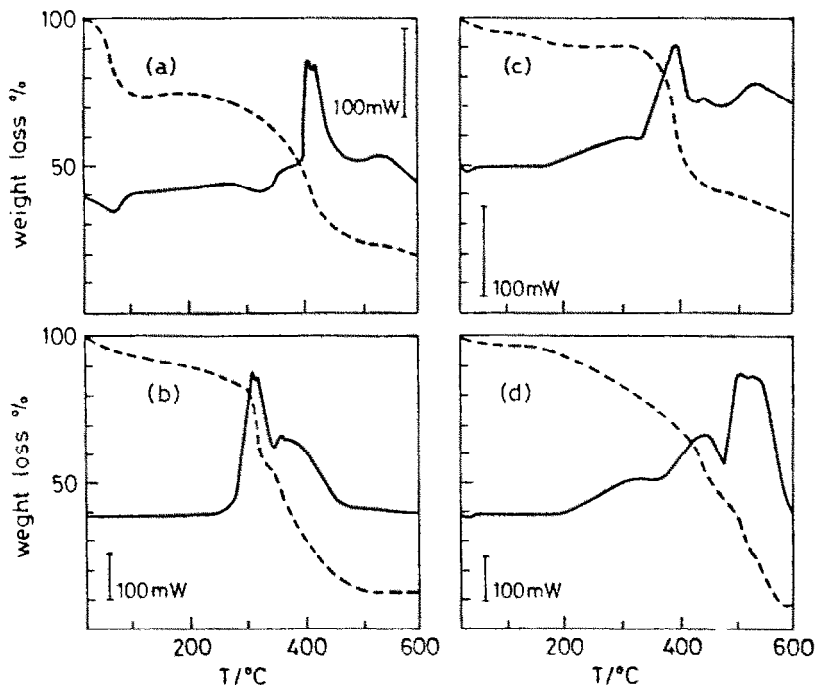


Fig. 5. TG (---) and DTA (—) traces under air flow: (a) resin A, (b) Mo-grafted resin A, (c) resin B, (d) Mo-grafted resin B.

Similar conclusions have been reached independently for the behaviour of boronic acid function [10]. This trend is equally apparent for the Mo-supported resins, though their thermal degradation spectra are much more complicated owing to the disruptive effect of molybdenum.

Fig. 2 can now be considered in greater detail. The slow loss of weight displayed by all samples at temperatures higher than 100 °C can be related to the observed modification of the IR spectra. It may therefore be deduced that the condensation pattern of the boronic groups follows a similar mechanism in both free and supported boronic acids [11], in spite of the difficulty of defining a clear-cut completion temperature for the latter.

Fig. 2a also evidences the high moisture content of the resin A. This weakly bonded water can be desorbed only partially by vacuum pumping at room temperature.

As far as degradation of the polymer network is concerned, weight loss onset temperature is lower than 300 °C for all samples and decomposition is virtually complete before 500 °C. The degradation patterns of resin B, as such and Mo-grafted (Figs. 2c and 2d, respectively), when the effects of the inorganic

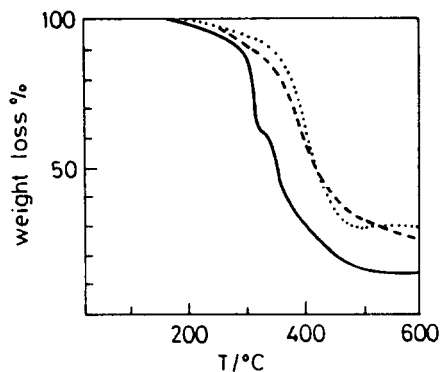


Fig. 6. TG traces of resin A: (····) under N_2 ; (- - -) under air; (—) Mo-grafted under air. Percent on anhydrous basis.

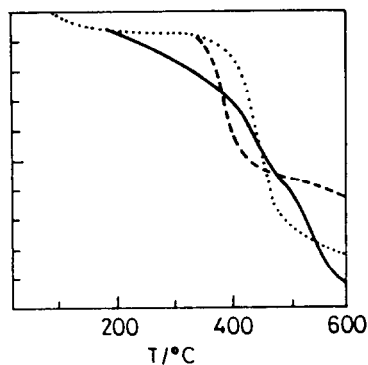


Fig. 7. TG traces of resin B: (····) under N_2 ; (- - -) under air; (—) Mo-grafted under air. Percent on anhydrous basis.

groups are taken into account, are in good agreement with the literature data for the thermal decomposition of polystyrene [12]. This behaviour suggests that neither the insertion of boronic acid nor the grafting of molybdenum significantly affects the stability of polystyrene under inert gas.

To observe modifications in the degradation pattern in the presence of oxygen, TG-DTA experiments were carried out under air flow. The results are reported in Fig. 5. The DTA traces are not shown on the same scale as in Fig. 1 in order to give the full details of each curve. For resins A and B as such, onset of degradation accompanied by a small endothermic effect can be observed slightly below 300 °C and the exothermic effect of autoxidation does not begin until a higher T is reached. By contrast, this effect accompanies the weight loss from its onset in the grafted resins.

The TG traces of the original resins heated in nitrogen and in air, and the Mo-functionalized resins heated in air are compared in Figs. 6 (resin A) and 7 (resin B). In the case of resin A, the passage from nitrogen (trace 1) to air (trace 2) corresponds to an increase in the onset temperature of the main weight loss. The insertion of molybdenum strongly decreases the temperature of degradation in air (trace 3).

Turning to resin B, under air flow the decomposition temperature decreases (trace 2 as compared to trace 1), but the formation of more stable intermediate slows down the degradation before it attains completion. Degradation of the grafted resin begins near 200 °C (trace 3), but its relative slowness corresponds to increased formation of stable intermediates.

The absence of any influence of molybdenum on the degradation pattern in

an inert atmosphere and the observed shift to a lower degradation temperature in air strongly suggests that Mo^{6+} has a specific catalytic role in oxidative degradation of the lattice.

The degradation onset temperature can be usefully employed as an indicator of thermal stability when considering which resin should be used as a catalyst support. The stabilities of resins A and B are very similar under an inert atmosphere, whereas A is more stable under oxidative conditions.

Further studies are needed to explain the higher destabilizing effect of molybdenum on resin B. One possibility is that molecular oxygen activated by Mo^{6+} reacts more easily with the weak links controlling the degradation of polystyrene than with the chain ends from which the unzipping reaction of polyacrylate proceeds [13].

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