Synthesis, characterization, and thermal stability of poly(N-maleyl glycine-co-N-vinylpyrrolidone)

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Received: 24 March 1997/Revised version: 10 June 1997/Accepted: 18 June 1997

SUMMARY

The free radical copolymerization of N-maleyl glycine (MG) with vinylpyrrolidone (NVP) was studied in the range from 10 to 90 mol% in the feed. Copolymer compositions obtained by elemental analysis reflect the monomer feed concentrations. The r₁ and r₂ were determined by the Fineman-Ross and Kelen-Tudos method. The experimental data indicate random comonomer incorporation with slightly alternating tendency. The thermogravimetric analysis of the copolymers showed high thermal stability in N₂.

INTRODUCTION

Maleimides and bismaleimides represent a class of thermoset resins with service temperatures around 200°C (1,2). Their acceptance as the next generation of matrix resins is mainly a result of their easy processability and retention of mechanical properties at high temperatures (3). Different types of maleimides have been synthesized previously with the aim of improving their fracture toughness. We have previously reported the thermal behavior of different polymers containing the maleimide moiety (4).

The technique of thermogravimetric analysis (TGA) has been widely used in polymer characterization in thermal stability and degradation studies. Kinetic parameters such as activation energy (E), pre-exponential factor (A), and reaction order (n) give a quantitative measurement of thermal stability (5).

This paper reports the synthesis, characterization, and thermal stability behavior of a new functional copolymer. The investigation also includes the variation of the kinetic parameters of the thermal degradation of copolymer samples with the type of substituent and with copolymer composition.

EXPERIMENTAL PART

Materials

N-vinylpyrrolidone (NVP) was obtained from Merck, Darmstadt, and distilled twice prior to use. N-Maleyl glycine (MG) was prepared according to published procedures (6).

Preparation of poly(N-maleyl glycine-co-N-vinylpyrrolidone), P(MG-co-NVP)

A volume of tetrahydrofuran was transferred to septum-capped, nitrogen purged flasks containing NVP (0.7 mmol), 0.6 mg initiator (AIBN), and 0.7 mmol of

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MG. The ampoule was sealed under vacuum \(10^{-3}\) mm Hg and the copolymerization was carried out at 70°C for 12 hours. The polymer was filtered off and washed with ether. It was collected and dried under vacuum to constant weight.

**Measurements**

The melting point was determined with a Büchi Unimelt. Elemental analyses were carried out by a Carlo Erba 1106 Analyzer. Thermal analysis was performed in nitrogen atmosphere at a heating rate of 10°C/min. Thermogravimetric data were obtained by using a Perkin Elmer TGS-1 Thermal Analyzer.

**RESULTS AND DISCUSSION**

*Synthesis and characterization of poly(N-maleyl glycine-co-N-vinylpyrrolidone)*

The five copolymers of MG with NVP were synthesized by varying the feed ratios of both monomers from 10 to 90 mol%.

The copolymers are partially soluble in hot water, methanol, dimethylsulphoxide, acetone, and chloroform.

The IR spectra (KBr, cm\(^{-1}\)) show the most characteristic absorption bands: 3400 v-OH, -COOH; 2900 v-CH, CH\(_2\); 1780 and 1750 v-C=O, imide; 1700 v-C=O, -COOH; 1620 v-C=O amide. Copolymer composition was determined from elemental analysis data (see Table 1), and determined as a function of feed composition. Reaction parameters and copolymer compositions are shown in Table 2. The relationship between mole percent MG incorporated into the copolymers and the comonomer feed ratio is shown in Fig. 1.

![Figure 1. Copolymerization composition curve of N-maleyl glycine (MG) with N-vinylpyrrolidone (NVP) at 70°C in dioxane.](image)