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

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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 r_1 and r_2 were determined by the Fineman-Ross and Kelen-Tüdos method. The experimental data indicate random comonomer incorporation with slightly alternating tendency. The thermogravimetric analysis of the copolymers showed high thermal stability in N_2.

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 ν-OH, -COOH; 2900 ν-CH, CH_2; 1780 and 1750 ν-C=O, imide; 1700 ν-C=O, -COOH; 1620 ν-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.

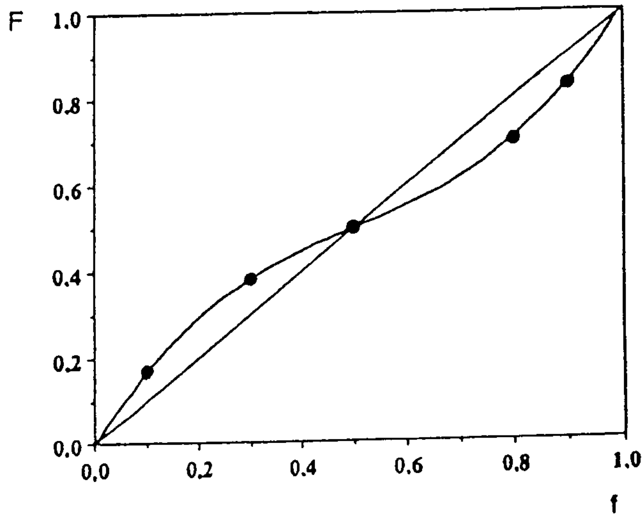

Figure 1. Copolymerization composition curve of N-maleyl glycine (MG) with N-vinylpyrrolidone (NVP) at 70°C in dioxane.

Table 1. Elemental analysis of the copolymers[a]

Copolymers	Initial composition (f)	(C)	C	(N)	N	(H)	H
1	0.1	62.3	61.7	12.0	11.9	7.0	8.1
2	0.3	57.9	58.7	11.3	10.5	6.3	5.5
3	0.5	54.0	52.3	10.5	10.0	5.3	5.5
4	0.8	49.2	48.1	9.6	9.2	4.0	4.6
5	0.9	47.8	48.0	9.3	9.2	3.6	4.0

a) In brackets the theoretical values

Table 2. Radical copolymerization of N-maleyl glycine (MG) with vinylpyrrolidone (NVP) at 70°C and 12 hours in dioxane.

Copolymer	(f) in MG	MG (mmol)	NVP (mmol)	AIBN (mg)	Dioxane (ml)	Yield (%)	m.p. (°C)	Copol. Comp. MG:NVP[a]
1	0.1	0.3	2.3	2.1	2.8	75.3	300	0.16:0.84
2	0.3	0.5	1.1	1.3	1.5	80.4	280	0.38:0.62
3	0.5	0.7	0.7	1.2	1.5	78.2	290	0.50:0.50
4	0.8	1.3	0.3	1.3	1.5	82.4	290	0.70:0.30
5	0.9	0.3	2.3	2.1	2.8	75.8	290	0.86:0.14
Homopolymer								
6	0.0	-	1.3	1.1	1.4	81.1	250	
7[b]	1.0	0.7	-	0.6	0.7	85.0	320	

[a] determined from elemental analyses

[b] previously published (11)

Determination of the monomer reactivity ratios

The monomer reactivity ratio values for the copolymerization of MG and NVP were determined from the monomer feed ratios and the copolymer composition. The Fineman-Ross (7), and Kelen-Tüdos (8) method were used to determine the monomer reactivity ratios. The Fineman-Ross method (see Table 3) yielded reactivity ratios for MG and NVP of $r_1 = 0.50$ and $r_2 = 0.52$, respectively; $r_1 x r_2 = 0.25$ (see Fig. 2). The Kelen-Tüdos method (see Table 4) gave reactivity ratios of $r_1=0.34$ and $r_2=0.31$, respectively; $r_1 r_2 = 0.105$ (see Fig. 3). The experimental data indicated a random comonomer incorporation with a slightly alternating tendency.

Table 3. Copolymerization reactivity ratios of poly(N-maleyl glycine-*co*-N-vinylpyrrolidone), P(MG-*co*-NVP), by the Fineman-Ross method.

$Y=m_1/m_2$	X_0	X_0/Y	$(Y-1)$	$X_0/Y(Y-1)$	X_0^2	X_0^2/Y
5.25	9.00	1.71	4.25	7.29	81.00	15.43
1.63	2.33	1.43	0.63	0.90	5.43	3.33
1.00	1.00	1.00	0.00	0.00	1.00	1.00
0.43	0.25	0.60	-0.57	-0.34	0.06	0.15
0.21	0.12	0.56	-0.80	-0.45	0.01	0.02

The values of the monomer reactivity ratios r_1 and r_2 determined by the Fineman-Ross method are higher than those by the Kelen Tüdos method. This may be attributed to that this method may involve large uncertainties in the slopes and, consequently, in the r_1 and r_2 values.

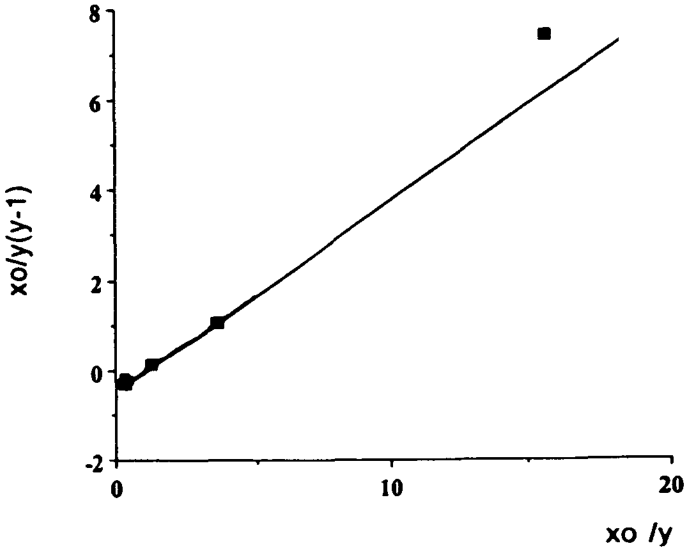

Figure 2. Data to calculate the monomer reactivity ratios for the poly(N-maleyl glycine-*co*-N-vinylpyrrolidone) copolymers by the Fineman-Ross method.

The Kelen-Tüdos equation symmetrically transforms into

$G = F \bullet r_1 - r_2$

by introducing the new parameters ξ, η, and α, where: $G = X_0/Y(Y-1)$ and $F = X_0^2/Y$; Monomers: M_1 = MG and M_2 = NVP; $\alpha = (F\min \times F\max)^{0.5}$; $\xi = F/(\alpha + F)$; $\eta = G/(\alpha + F)$

Table 4. Copolymerization reactivity ratios of poly(N-maleyl glycine-*co*-N-vinylpyrrolidone), P(MG-*co*-NVP), by the Kelen Tüdos method, μ = 1.396396, α = 0.9290.

f	M_1	M_2	W	P_1	ξ	η
0.10	1.17	0.14	40.4	84	0.964	0.354
0.33	1.12	0.48	48.4	62	0.831	0.188
0.50	0.70	0.70	48.2	50	0.510	0.000
0.80	0.32	1.28	43.5	30	0.085	-0.249
0.90	0.14	1.17	42.5	17	0.036	-0.335

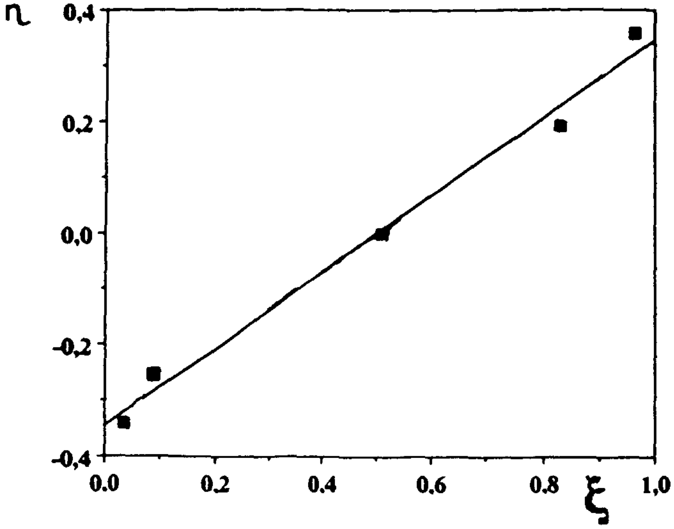

Figure 3. Data for the calculation of the monomer reactivity ratios for the poly(N-maleyl glycine-*co*-N-vinylpyrrolidone) copolymers by the Kelen-Tüdos method.

Thermal stability of the P(MG-co-NVP) copolymers

The thermal stability of the copolymers was studied by programmed thermogravimetric analysis over a temperature range from 20 to 500°C under nitrogen (see Fig. 4).

The thermograms obtained show that the polymers degrade in a single-stage process which is characteristic for the thermal decomposition of a great number of macromolecules and gives evidence that no other competitive and simultaneous processes occur (12).

Fig. 4a shows the thermogravimetric curves of the copolymers P(MG-*co*-NVP), which degrade in a single-stage process except of P(MG-*co*-NVP), sample 1, with 0.18 mol of MG in the copolymer which degrades apparently in a two stage process.

Fig. 4b shows the thermogravimetric curves of the polymers P-MG and P-NVP, which degrade in a single-stage process.

Table 5 shows the values of the TDT for each copolymer which were taken from the first strong change in the slope of the thermogravimetric curve (see Fig. 4).

The TDT values of the copolymers showed that copolymer 1 with the lower MG comonomer unit has a higher value of TDT. The copolymers exhibit lower TDT than the homopolymers (Table 5). The main reason may be attributed to that the linear P(MG-*co*-NVP) presents in its structure a percentage of intramolecular crosslinking.

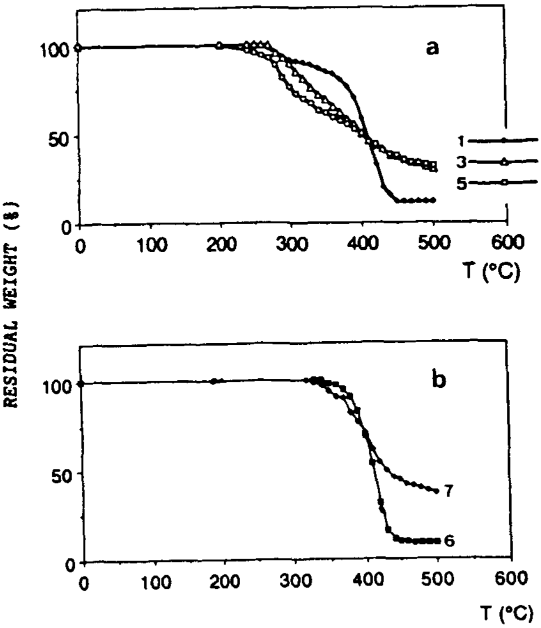

Figure 4. TG curves of the copolymers (samples 1, 3, 5) (a), and both homopolymers (b). Heating rate: 10°C/min, under nitrogen.

Table 5. Thermal behavior and decomposition temperatures TDT of the copolymers and homopolymers.

Copolymer No.	Weight loss (%) at different temperatures (K)					
	373	473	573	673	773	TDT(K)
1	0.0	0.0	6.3	39.7	88	543
3	0.0	0.0	22.9	48.8	66	523
5	0.0	0.0	10.7	48.8	68	543
Homopolymer						
6	0.0	0.0	0.0	30.9	90	623
7	0.0	0.0	0.0	28.1	65	593

Kinetic parameters for the thermal degradation of the polymers

Kinetic parameters such as the pre-exponential factor (A), activation energy (E) and reaction order (n) were evaluated according to the following general equation:

$$\beta = \ln [-d\alpha/dt/v(1 - \alpha)^n] = \ln A - E/RT$$

where: $-(d\alpha/dt) = K_n(1 - \alpha)^n$, α = fraction of sample weight reacted at time t, n = reaction order, and K_n = specific rate.

The reaction rate $d\alpha/dt$ was calculated using a differential technique and taking account of the heating rate (10°C/min), using data from plots of temperature vs. sample weight fraction (4). The specific rate K_n was obtained using the

Arrhenius relation. The general equation was obtained by combining the equations, and incorporating v to the logarithmic form.

A linear multiple regression program was developed on the kinetic equation described previously (4, 9-11) to calculate the kinetic parameters A and E from a linear least-squares fit of the data in a semilogarithmic plot β vs 1/T (see Fig. 5). The zero-order model was the best fit for the kinetic data of each polymer derived from the plot. The data are summarized in Table 6. The linearity of each plot was good with a correlation of 0.990 to 0.999. The activation energy of the copolymers was lower than that for the homopolymers, and the highest was for copolymer 3. The incorporation of the MG unit into the copolymer decreased the E, the trend is the same as for the TDT values.

Table 6. Kinetic parameters of thermal decomposition for copolymers and homopolymers.

Copolymer P(MG-*co*-NVP)	f MG	A (s^{-1})	TDT (°K)	E Kcal/mol	n	Copol. comp. MG:NVP
1	0.1	3.2×10^{1}	573	13.1	0	0.16:0.84
3	0.5	5.3×10^{-2}	523	9.1	0	0.50:0.50
5	0.9	57×10^{-2}	543	9.5	0	0.83:0.17
Homopolymer						
P-MG	1.0	44×10^{1}	593	20.1	0	
P-NVP		14×10^{3}	623	28.0	0	

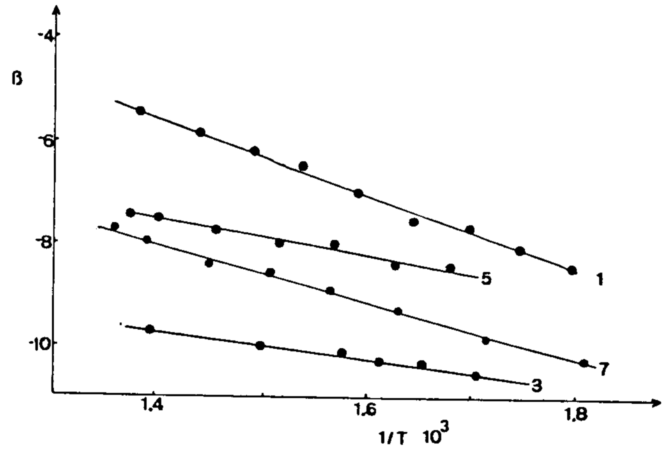

Figure 5. Arrhenius plot for the thermal degradation of poly(N-maleyl glycine-*co*-N-vinylpyrrolidone), samples 1, 3 and 5, and the poly(N-maleyl glycine), 7.

CONCLUSIONS

The thermal decomposition temperatures of poly(N-maleyl glycine-*co*-N-vinylpirrolidone) copolymers are influenced by the composition of the copolymer. The incorporation of MG decreases the TDT values. The kinetic parameters also show the same trend and obey zero-order kinetics.

The residue of copolymers 1, 2 and 3 were approximately 10% and 30%, respectively, at 500°C. They show a similar thermal behavior like that of the homopolymers.

Finally, the activation energy values obtained for the copolymers are lower than those of the homopolymers which could mean that the influence of both comonomeric units is great and the thermal stability was decreased by a higher incorporation of MG into the backbone.

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