

Preparation and Characterization of the Copolymer Containing *N*-Pyridyl Bi(methacryl)imide Unit

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ABSTRACT: The copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide was prepared based on the reaction of polymethacrylic acid with 2-pyridylamine. The molecular structure was characterized by ¹H-NMR, FTIR, UV-Vis, and circular dichroism techniques. The physical properties of polymethacrylic acid change significantly after an introduction of 6 mol % *N*-2-pyridyl bi(methacryl)imide unit. In particular, the thermal degradation of the polymer was systematically studied in flowing nitrogen and air from room temperature to 800°C by thermogravimetry at a constant heating rate of 10°C/min. In both atmospheres, a four-stage degradation process of the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide was revealed. The initial thermal degradation temperature T_{d1} and the first, second, and third temperatures at the maximum weight-loss rate T_{dm1} , T_{dm2} , and

T_{dm3} all decrease with decreasing sample size or changing testing atmosphere from nitrogen to air, but the fourth temperature at the maximum weight-loss rate T_{dm4} increases. The maximum weight-loss rate, char yield at elevated temperature, four-stage decomposition process, and three kinetic parameters of the thermal degradation were discussed in detail. It is suggested that the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide exhibits low thermal stability and multistage degradation characteristics. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1673–1678, 2002

Key words: copolymerization; *N*-2-pyridyl bi(methacryl)imide-containing polymer; chain; thermogravimetric analysis (TGA); thermal properties

INTRODUCTION

Poly(cyano-/alkoxy-/alkyl-biphenyl methacrylate) as a side-chain liquid crystalline polymer with versatile properties has received increasing attention.^{1–3} There have also been a few investigations on the synthesis of 2-pyrimidyl acrylamide copolymer,⁴ *p*-*n*-diblock copolymer containing a bipyridylene unit,⁵ and poly(butyl methacrylate-*co*-vinylpyridine),⁶ and on gas permselectivity through polyvinylpyridine,^{7,8} which could be one of the good gas-separation membranes. The polyvinylpyridine crosslinked by divinylbenzene has been widely used as an ion exchanger. That is to say, most of the pyridine ring-containing polymers always behave with the versatility that makes them useful in numerous functions. Therefore, they have been extensively investigated recently. However, no reports concerning the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide have been found.

No data about the molecular structure characterization, thermal degradation, and kinetics of the copolymer have yet been reported in the literature. In this study, the copolymer was synthesized through the modification of polymethacrylic acid with 2-pyridylamine and characterized by proton NMR, IR, UV-Vis, and circular dichroic techniques. In particular, the thermal decomposition characteristics and activation energy of the copolymer in nitrogen and air were studied systematically for the first time.

EXPERIMENTAL

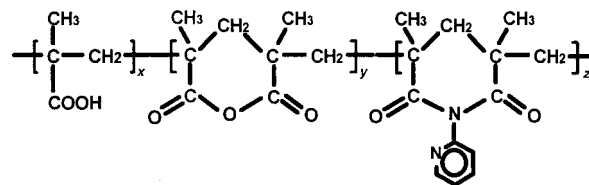
Polymethacrylic acid with molecular weight of 100,000 (CAS no. 25087-26-7) was obtained from Polysciences (Warrington, PA). The copolymer was prepared by dissolving polymethacrylic acid (1 g) in tet-

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Scheme 1 The copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide.

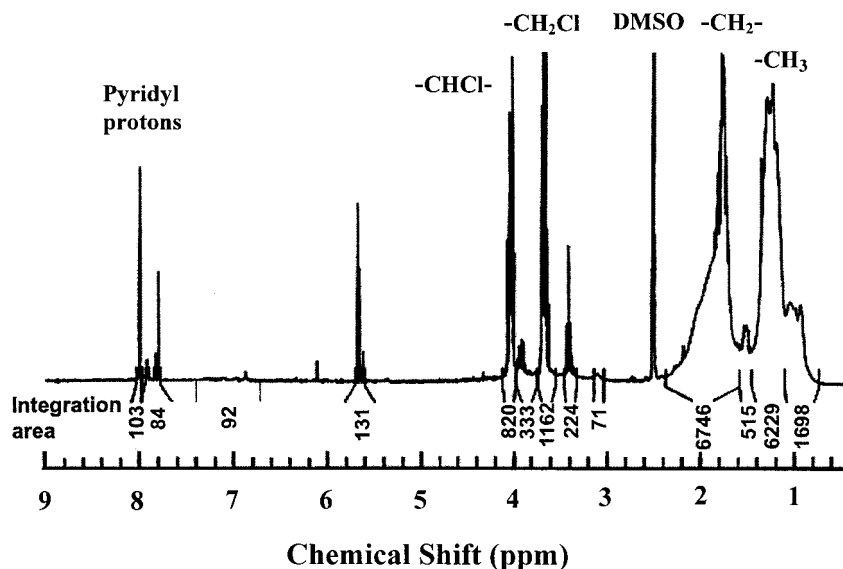


Figure 1 Proton NMR spectrum of the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide in DMSO-*d*₆ at 300.13 MHz after scan number 533.

rahydrofuran (5 mL). After the polymethacrylic acid solution was heated at 55°C and maintained for 30 min, PCl₃ (1 mL) was added dropwise. 2-Pyridylamine (1.5 g) was added in four steps into the mixture every 3 min. Then triethylamine (2 mL) was added as catalyst. Finally, PCl₃ (4 mL) was added

again. This reaction solution was refluxed for 20 h and cooled to room temperature, after which 50 mL water was added to precipitate the product. An orange copolymer was obtained after filtration, with a yield of about 60%. The copolymer is structurally depicted in **Scheme 1**.

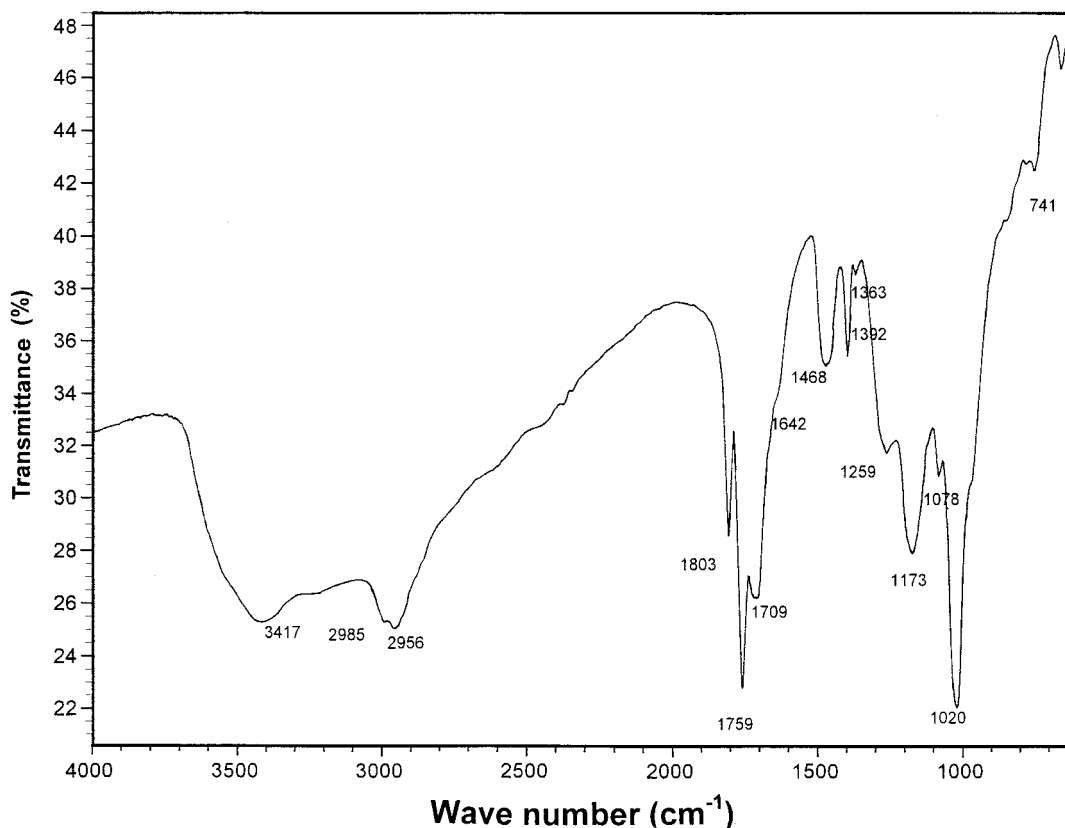


Figure 2 FTIR spectrum of solid copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide in KBr.

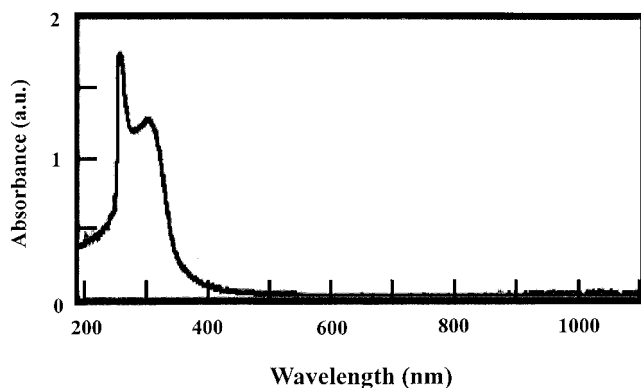


Figure 3 UV-Vis spectrum of dilute solution of the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide in DMSO.

The $^1\text{H-NMR}$ spectrum was obtained in deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) using a Bruker MSL-300 spectrometer (Bruker Instruments, Billerica, MA) operated at 300.13 MHz. The FTIR spectrum was recorded on a Nicolet Magna 550 FTIR spectrometer (Nicolet Instruments, Madison, WI) at 2 cm^{-1} resolution on KBr pellet. The UV-Vis spectrum of the dilute solution in DMSO was obtained on a U-3000 spectrophotometer (Hitachi, Tokyo, Japan). The circular dichroism spectrum of the dilute DMSO solution of the polymer was recorded at 30°C in a flowing nitrogen on a Jasco J-715-150S circular dichroism spectropolarimeter (Jasco, Tokyo, Japan) at bandwidth 2 nm, sensitivity 20 mdeg, resolution 0.2 nm, response 0.5 s, accumulation 2, and scanning speed 100 nm/min. Thermogravimetry was carried out with samples of 1.8–2.9 mg at a heating rate $10^\circ\text{C}/\text{min}$ in flowing nitrogen and flowing air (80 mL/min) by the use of a Perkin-Elmer 7 series thermal analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT).

RESULTS AND DISCUSSION

The $^1\text{H-NMR}$ spectrum of the copolymer

The $^1\text{H-NMR}$ spectrum of copolymer in deuterated DMSO is characterized by three main signals, which

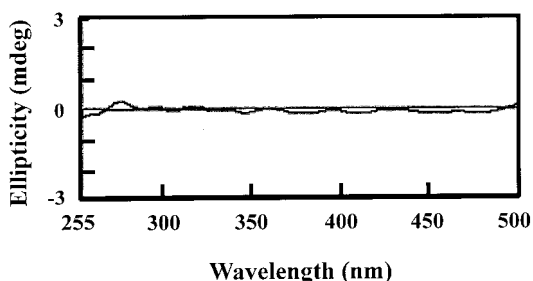


Figure 4 Circular dichroism spectrum of dilute solution of the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide in DMSO at 30°C .

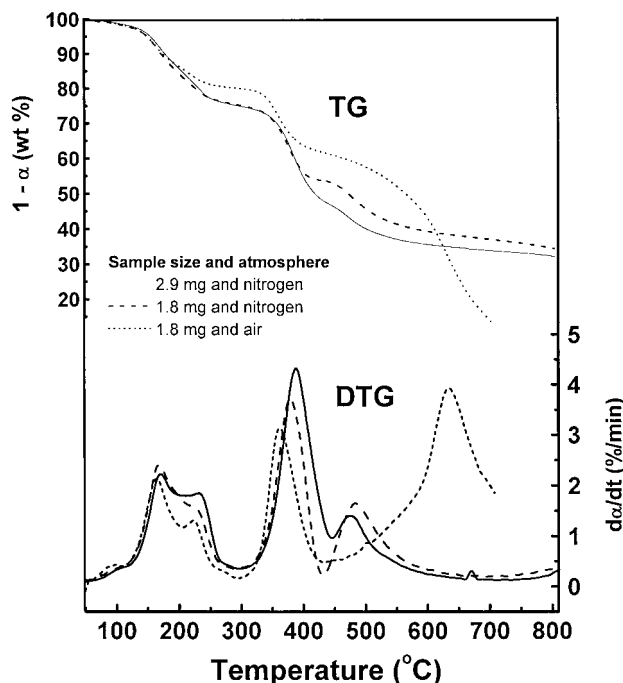


Figure 5 TG and DTG curves of the copolymer of methacrylic acid anhydride and *N*-2-pyridyl bi(methacryl)imide with the sample mass and atmosphere: (—) 2.9 mg and nitrogen; (---) 1.8 mg and nitrogen; (···) 1.8 mg and air, at a heating rate of $10^\circ\text{C}/\text{min}$.

correspond to the three types of protons on the polymer chains, as shown in Figure 1. A strong peak between 0.93 and 1.35 ppm should be attributed to $-\text{CH}_3$ groups; another strong peak centered at 1.77 ppm is ascribed to the $-\text{CH}_2-$ protons in the main chain; and the four singlets at 7.79–8.00 ppm and weak peaks ranging from 6.13 to 7.35 ppm are attributed to the aromatic protons on the pyridyl ring.^{9–11} The peak at 5.67 ppm might be related to the protons on the double bonds.⁴ It can be seen that the imidization degree of polymethacrylic acid by pyridylamine is not high. Based on a comparison of the peak areas of pyridyl protons with methyl protons [i.e., eq. (1)], the imidization degree is about 6 mol %.

Degree of imidization =

$$\frac{(\text{Integration area of pyridyl protons}) \times 2.5}{\text{Integration area of methyl protons}} \times 100\% \quad (1)$$

Note that the peaks at 3.67 and 4.04 ppm could be attributable to $-\text{CHCl}-$ and $-\text{CH}_2-\text{Cl}$ protons, respectively, which formed by the chlorination of $-\text{CH}_2-$ and $-\text{CH}_3$ units by the PCl_3 .

The IR spectrum of the copolymer

The IR spectrum of the copolymer is shown in Figure 2. It exhibits the strongest bands at 1020 cm^{-1} , attrib-

TABLE I
Thermal Degradation Characteristics of the Copolymer of Methacrylic Acid Anhydride and 2-Pyridyl Bi(methacryl)imide

Sample size (mg)	Atmosphere	$T_d/T_{dm1}/T_{dm2}/T_{dm3}/T_{dm4}$ (°C)	$(d\alpha/dt)_m$ 1st/2nd/3rd/4th stage (% min ⁻¹)	Char yield at 700°C (wt %)
2.9	Nitrogen	143/170/232/389/470	2.2/1.8/4.4/1.4	33.7
1.8	Nitrogen	141/168/224/379/481	2.4/1.6/3.8/1.7	37.1
1.8	Air	137/163/223/362/633	2.1/1.3/3.2/4.0	14.9

uted to C—O stretching vibration; at 1759 and 1709 cm⁻¹, assigned to C=O stretching vibration; and the broadest peak, centered at 3417 cm⁻¹, attributed to O—H asymmetrical stretching vibration in the carboxyl groups. A broad double peak at 2956 and 2985 cm⁻¹ should be attributable to C—H symmetrical stretching vibration in the —CH₂— and —CH₃ groups. A medium band at 1803 should be attributed to anhydride (CO—O—CO) group and the medium bands at 1173 and 1259 cm⁻¹, to C—O—C asymmetrical stretching and also imide vibrations. There are also several medium peaks at 1392 cm⁻¹ assigned to typical C—N stretching vibration in the imide group,¹² at 1468 cm⁻¹ assigned to the stretching vibration of the pyridine ring, and at 741 cm⁻¹ assigned to C—H twisting (out-of-plane) vibration in the pyridyl ring.

The UV-Vis and circular dichroism spectra of the copolymer

Figure 3 shows a strong and sharp UV-Vis absorption peak, which is attributed to the presence of the pyridine ring in the copolymer. To obtain some information on the conformation of the copolymer in DMSO, the circular dichroism spectrum was measured and is shown in Figure 4. The circular dichroism spectrum shows the most intense positive (234 nm), the second most intense negative (190 nm), medium positive (206 nm), and weak negative (219 nm) peaks that originate from the asymmetrically arranged molecular structure. A split Cotton effect, centered at 199 nm, implies that the copolymer backbone has a regular asymmetric conformation and strong chiral conformation. The NMR, IR, and UV-Vis results indicate that the pyridylamine unit was connected to the macromolecular chain by an imide group, although its content was not high. Note that original polymethacrylic acid is a fine,

white powder and soluble in water but an introduction of only 6 mol % 2-pyridyl bi(methacryl)imide unit can make the polymethacrylic acid become an orange particle and insoluble in water, which is the major difference in properties of the synthesized copolymer and polymethacrylic acid.

Thermal degradation behavior of the copolymer

The thermogravimetry (TG) curves and derivative thermogravimetry (DTG) curves of the copolymer in nitrogen and air are shown in Figure 5. Four types of important decomposition parameters, the characteristic degradation temperature (T_d), the temperature at the maximum weight-loss rate (T_{dm}), the maximum weight-loss rate $(d\alpha/dt)_m$, and char yield at 500°C, are summarized in Table I. There is no significant weight loss until 140°C for the copolymer, indicating that the polymer exhibits low thermostability, possibly arising from easy abstraction of methyl, carboxyl groups, and water between two neighbor carboxyl groups and formation of anhydrides on the copolymer chain. The thermal degradation behavior of the polymer varies with the testing sample mass and atmosphere. With increasing sample mass, most of the degradation temperatures (T_d , T_{dm1} , T_{dm2} , T_{dm3}) increase, whereas $(d\alpha/dt)_{m1}$ and $(d\alpha/dt)_{m2}$ decrease. This appears to be evidence illustrating a diffusion-controlled process of the thermal degradation process of the copolymer. A similar relationship between degradation characteristics and sample mass has been observed for the degradation of poly(*N*-phenyl methacrylamide).¹³ The degradation temperatures (T_d , T_{dm1} , T_{dm2} , T_{dm3}), $(d\alpha/dt)_{m1}$, $(d\alpha/dt)_{m2}$, $(d\alpha/dt)_{m3}$, and char yield at 700°C are all higher, whereas T_{dm4} and $(d\alpha/dt)_{m4}$ are much lower in nitrogen than those in air, possibly because of oxida-

TABLE II
Temperature Range and Weight Loss of Each Degradation Step for the Copolymer of Methacrylic Acid Anhydride and 2-Pyridyl Bi(methacryl)imide

Sample size (mg)	Atmosphere	Temperature range (°C)	Weight loss (wt %)
		1st/2nd/3rd/4th stage	1st/2nd/3rd/4th stage
2.9	Nitrogen	100–209/209–299/299–445/445–700	14.7/9.7/28.8/14.6
1.8	Nitrogen	100–208/208–298/298–430/430–700	16.6/8.5/21.2/19.8
1.8	Air	100–205/205–299/299–436/436–700	13.5/6.3/18.3/48.8

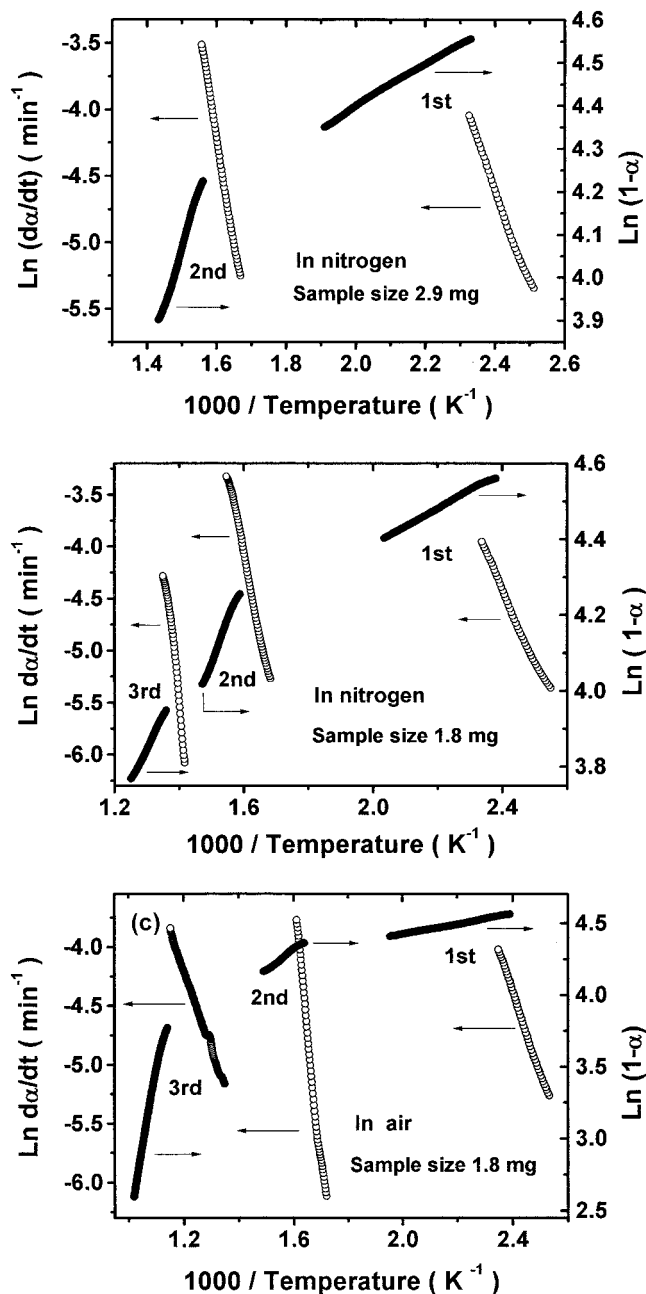


Figure 6 Application of the Friedman method to the TG and DTG data obtained for the copolymer of methacrylic acid anhydride and 2-pyridyl bi(methacryl)imide at the sample mass and atmosphere [(a) 2.9 mg and in nitrogen; (b) 1.8 mg and in nitrogen; (c) 1.8 mg and in air] for the calculation of activation energy (○) and reaction order (●) of thermal decomposition.

tive degradation from oxygen in air. These results imply a higher thermostability, faster initial degradation rate, but slower final degradation rate in nitrogen than in air.

Thermal degradation process of the copolymer

As listed in Table II, the temperature ranges of four-step decomposition of the copolymer in nitrogen and

air are almost independent of testing sample mass and atmosphere, suggesting that their thermal process is similar. The weight losses corresponding to the first three-stage decomposition vary slightly with testing sample mass and atmosphere; however, the weight losses corresponding to the fourth-stage decomposition vary significantly with changing test atmosphere. This variation in weight loss must be the result of the oxidative decomposition from oxygen in air. The first-stage decomposition of copolymer could be corresponding to the exclusion of water and/or methyl group (theoretical weight loss = 10.5 and 17.4%, respectively) and subsequent crosslinking between the polymer chains. The average theoretical weight loss of 14.0% is close to the weight loss of the first stage listed in Table II, implying that the first stage may be attributed to both water exclusion and methyl exclusion. The second-stage decomposition might be attributed to the exclusion of carbon dioxide and carbon monoxide from residual carboxyl and anhydride (CO—O—CO) groups. The theoretical carboxyl and anhydride group content should range from 46 to 52 wt %, whereas the carbon oxide content from the copolymer was 6.3–9.7 wt %, implying an uncompleted exclusion of the carboxyl group. The third-stage decomposition may correspond to major thermal pyrolysis of the polymer's main chain, and the fourth-stage decomposition may correspond to the pyrolysis of residual char in nitrogen and the oxidative pyrolysis of the residual in air.

Thermal degradation kinetics of the copolymer

Plots for the calculation of activation energy of the degradation of the copolymer, created by Friedman and

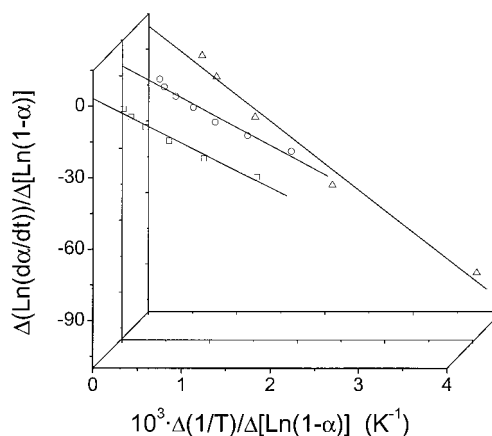


Figure 7 Application of the Freeman-Carroll method to the TG and DTG data obtained for the copolymer of methacrylic acid anhydride and 2-pyridyl bi(methacryl)imide with the sample mass and atmosphere [(□) 2.9 mg and nitrogen; (○) 1.8 mg and nitrogen; (△) 1.8 mg and air] for the calculation of activation energy of their major thermal decompositions.

TABLE III
Kinetic Parameters of the Thermal Decomposition of the Copolymer of Methacrylic Acid Anhydride and 2-Pyridyl Bi(methacryl)imide

Sample size (mg)	Atmosphere	Friedman method			Freeman–Carroll method
		1st stage $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)	3rd stage $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)	4th stage $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)	3rd stage $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)
2.9	Nitrogen	57/14.0/13	129/6.5/24	—	154/3.1/27
1.8	Nitrogen	55/14.5/13	119/7.0/22	196/14.3/38	162/4.1/29
1.8	Air	58/19.6/14	191/16.6/38	56/0.7/5.0	239/9.6/45

Freeman–Carroll techniques,^{9,14,15} are shown in Figures 6 and 7, respectively. The calculated activation energy data are summarized in Table III. It is obvious that the degradation activation energy and frequency factor for the copolymer are lower than those for most thermally stable polymers in both atmospheres,^{10,11,16,17} although the decomposition order for the copolymer is higher than that for the thermostable polymers. The activation energy, decomposition reaction order, and frequency factor of the first- and second-step degradation for copolymer are substantially independent of testing sample mass, and are lower in nitrogen than in air. The activation energy and frequency factor values calculated by the Friedman technique are also lower than those calculated by the Freeman–Carroll technique. Very similar phenomena have been observed for the decomposition of poly(*N*-phenyl methacrylamide).¹³ All of these suggest the lower thermostability of the copolymer.

CONCLUSIONS

The molecular structure of the copolymer has been characterized by proton NMR, IR, UV–Vis, and circular dichroism techniques. An introduction of 6 mol % *N*-2-pyridyl bi(methacryl)imide unit makes the poly-methacrylic acid become an orange particle and insoluble in water. Its thermal stability, determined by TG technique, is lower and the degradation occurs in four steps in both nitrogen and air. The kinetic parameters of thermal decomposition of the copolymer show a dependency of testing atmosphere and calculating technique, suggesting that the thermal degradation mechanism varies with the atmosphere.

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