

Structure and Thermal Degradation of Poly(*N*-phenyl acrylamide) and Poly(*N*-phenyl methacrylamide)

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ABSTRACT: Poly(*N*-phenyl acrylamide) (PPA) and poly(*N*-phenyl methacrylamide) (PPMA) were prepared by using *N*-phenyl acrylamide and *N*-phenyl methacrylamide as monomer, respectively, in tetrahydrofuran using azobisisobutyronitrile as initiator. FT-IR, ¹H-NMR, and GPC were used to characterize their molecular structure. The PPA obtained exhibited higher molecular weight and wider molecular weight distribution than that of PPMA. Their thermal degradation and kinetics were systematically investigated in two atmospheres of nitrogen and air from room temperature to 800°C by thermogravimetric analysis at 10°C/min. Based on the thermal decomposition reactions in nitrogen and air, it is shown that a three-step degradation process in nitrogen

and a four-step degradation process for two polymers were observed in this investigation. The initial thermal degradation temperature was lower than 190°C. Under two atmospheres, PPA exhibits higher degradation temperature, higher temperature at the maximum weight-loss rate, faster maximum weight-loss rates, and larger weight loss for the first-stage decomposition, as well as higher char yield at 500°C than those of PPMA. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1065–1071, 2003

Key words: poly(*N*-phenyl acrylamide); poly(*N*-phenyl methacrylamide); thermogravimetric analysis (TGA); thermal properties; decomposition kinetics

INTRODUCTION

Poly(cyano-biphenyl (meth)acrylate) and poly(alkoxy-biphenyl (meth)acrylate) as side-chain liquid crystalline polymers, characterized by versatile properties and a wide range of application potentials, have been the focus of increasing attention.^{1–3} Poly(*N*-cyano-biphenyl (meth)acrylamide) and poly(*N*-alkoxy-biphenyl (meth)acrylamide) are also believed to exhibit thermotropic liquid crystallinity and other important properties.³ We maintain that the properties of the polyacrylamides may be greatly manipulated by varying the substituents on the nitrogen atoms, to offer exciting possibilities for the development of new polymers. Although numerous investigations on the synthesis, structure, properties, and applications of the

liquid crystalline poly(cyano-biphenyl (meth)acrylate) and poly(alkoxy-biphenyl (meth)acrylate) are cited in the literature,³ only a few studies on the synthesis of poly(*N*-cyano-/alkoxy-biphenyl (meth)acrylamide), *N*-2-pyrimidyl, and *N*-2-pyridyl acrylamide copolymers have been reported.^{3–5} Furthermore, very few reports concerning poly(*N*-phenyl (meth)acrylamide) have been found. To our knowledge no data about the thermal degradation and kinetics of poly(*N*-phenyl (meth)acrylamide) have been reported in the literature. Therefore, the synthesis and molecular structure of the polyacrylamides, which are closely related to their performance and applications, are not sufficiently well understood. A better understanding of the structure and properties of the polyacrylamides is absolutely essential. In this study, poly(*N*-phenyl acrylamide) (PPA) and poly(*N*-phenyl methacrylamide) (PPMA) were synthesized and characterized by FT-IR, ¹H-NMR, and GPC techniques. In particular, the thermal decomposition characteristics and activation energy of the PPA and PPMA in nitrogen and air were studied systematically for the first time.

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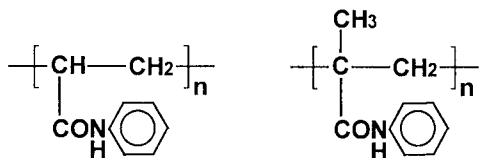
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EXPERIMENTAL

All monomers, solvents, and other chemicals were analytical reagents and used as received without fur-



Scheme 1 Poly(*N*-phenyl acrylamide) (PPA) and poly(*N*-phenyl methacrylamide) (PPMA).

ther purification. *N*-Phenyl acrylamide (PA) and *N*-phenyl methacrylamide (PMA) were prepared from acrylic acid and methacrylic acid as raw materials, respectively. Acryloyl chloride (0.12 mol, 8.3 mL) in 25 mL tetrahydrofuran was slowly added to a stirred cold (0–5°C) solution of aniline (0.1 mol, 9.2 mL) and triethylamine (0.1 mol, 13.9 mL) as catalyst in 50 mL tetrahydrofuran. The mixture was magnetically stirred for 20 h at room temperature and then filtered, after which a light yellow filtrate was obtained. The filtrate was purified by distillation at a reduced pressure (~ 0.05 MPa) for 4 h, after which a yellowish brown liquid product PA was obtained. Similarly, solid PMA was obtained when acryloyl chloride was replaced by methacryloyl chloride (0.12 mol). PPA as a gummy solid was obtained by PA solution polymerization in tetrahydrofuran in an 85–90°C water bath in the presence of azobisisobutyronitrile for 10 h. PPMA was prepared by PMA solution polymerization in tetrahydrofuran in a 65°C water bath with azobisisobutyronitrile as an initiator for 35 h. Scheme 1 shows the structures of PPA and PPMA.

The FT-IR spectrum was recorded on a Nicolet Magna 550 FT-IR spectrometer (Nicolet Instruments, Madison, WI) at a resolution of 2 cm⁻¹ on KBr pellets. A ¹H-NMR spectrum was obtained in deuterated dimethylsulfoxide using a Bruker MSL-300 spectrometer (Bruker Instruments, Billerica, MA) operated at 300.13 MHz. GPC experiments were carried out on a Waters 150C (Waters Associates, Milford, MA) with a composite column at 35°C with a refractometer and tetrahydrofuran as detector and solvent, respectively, at an elution rate of 1.0 mL/min. The composite column consisted of a linear μ -Styragel column and two non-linear μ -Styragel columns with pore diameters of 10,000 and 100 nm, respectively. The linear μ -Styragel column covered the molecular weights ranging from 2000 to 8,000,000. Polystyrene samples having known molecular weight were employed to make the calibration curve, elution time–molecular weight relationship. Thermogravimetric analysis was carried out at a heating rate of 10°C/min with the sample size of 1.8 mg for PPMA in flowing nitrogen (80 mL/min) and flowing air (80 mL/min) using a Perkin–Elmer 7 series thermal analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). Thermogravimetric analysis of the PPA was performed under the same conditions except for

the measurement in flowing air with the different sample size of 2.9 mg for the PPA.

RESULTS AND DISCUSSION

FT-IR spectrum of the PPMA

The FT-IR spectrum for PPMA is shown in Figure 1. Several characteristic bands were assigned as follows: the strongest sharp band at 1437 cm⁻¹ was attributed to the C–N stretch vibration. The second strongest bands at 1525, 1498, and 1597 cm⁻¹ were attributed to C–C ring-stretching vibration of benzene. A band at 1310 cm⁻¹ corresponded to C–N and N–H stretching vibration. The strong band at 1673 cm⁻¹ was attributed to the C=O stretching vibration. A broad band at 3350 cm⁻¹ corresponded to the N–H asymmetrical stretching vibration of the second amide. Two weak peaks at 2929 and 2982 cm⁻¹ were attributed to C–H symmetrical and asymmetrical stretching on CH₂ and CH₃ groups, respectively. A weak peak at 3057 cm⁻¹ was attributed to the C–H stretching vibration on the benzene ring. A band at 752 cm⁻¹ was ascribed to C–H out-of-plane wagging vibration from the substituted benzene ring and a band at 508 cm⁻¹ was attributed to C–C twisting vibration of the phenyl ring.

¹H-NMR spectrum of PPMA

The ¹H-NMR spectrum of PPMA in deuterated DMSO was characterized by four main signals, which exactly corresponded to the four types of protons on the polymer chains. A detailed assignment of the resonance peaks is shown in Figure 2. A strong triplet at 1.032 ppm was attributed to –CH₃ groups, the broad peak centered at 1.95 ppm was attributed to the –CH₂– protons, and the three singlets at 7.0–7.7 ppm were attributed to aromatic protons on the phenyl ring. A weak peak at 9.05 ppm was attributed to the –NH–proton.⁴ A combination of IR with ¹H-NMR spectra confirmed the presence of the macromolecular struc-

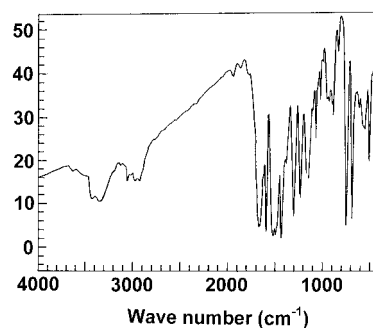


Figure 1 FT-IR spectrum of poly(*N*-phenyl methacrylamide).

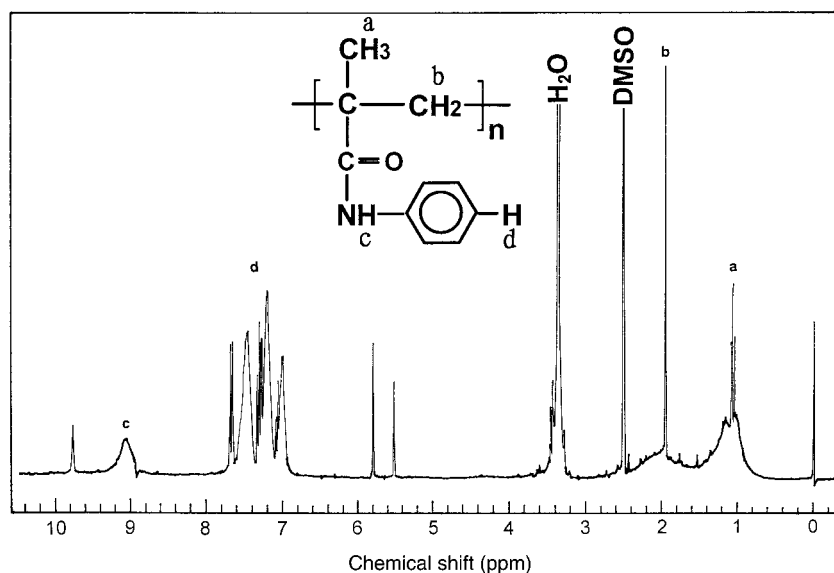


Figure 2 $^1\text{H-NMR}$ spectrum of poly(*N*-phenyl methacrylamide) in deuterated dimethylsulfoxide at 300.13 MHz after scan number 142.

ture of poly(*N*-phenyl methacrylamide) (PPMA) shown in Scheme 1.

Molecular weight and its distribution

The GPC traces of the PPA and PPMA are shown in Figure 3. The number-average molecular weight, Z-average molecular weight, and polydispersity of the PPA are 80,500, 1,070,600, and 4.4, respectively, whereas the two corresponding molecular weights and polydispersity of the PPMA are all lower (46,600, 618,000, and 3.0, respectively). Additionally, the shapes of the GPC peaks are quite different. A long tail in the range of high molecular weight is observed for the PPA, indicating that there are so many fractions of higher molecular weight in the PPA. On the contrary, only a short tail of low molecular weight is found for the PPMA.

Thermal degradation behavior

The thermogravimetry (TG) curves and derivative thermogravimetry (DTG) curves of the PPA and

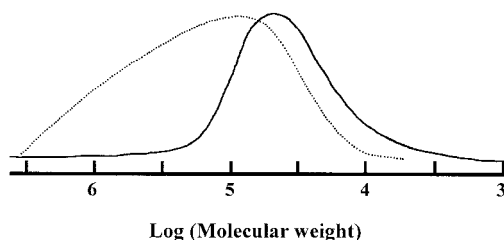


Figure 3 Gel permeation chromatograms of poly(*N*-phenyl methacrylamide) (—) and poly(*N*-phenylacrylamide) (···) with tetrahydrofuran as solvent.

PPMA in nitrogen and air are shown in Figures 4 and 5, respectively. Important types of decomposition parameters, the characteristic degradation temperature (T_d), the temperature at the maximum weight-loss rate (T_{dm}), the maximum weight-loss rate $(d\alpha/dT)_{mv}$, and char yield at 500°C, are summarized in Table I. The degradation temperature T_d was determined by ex-

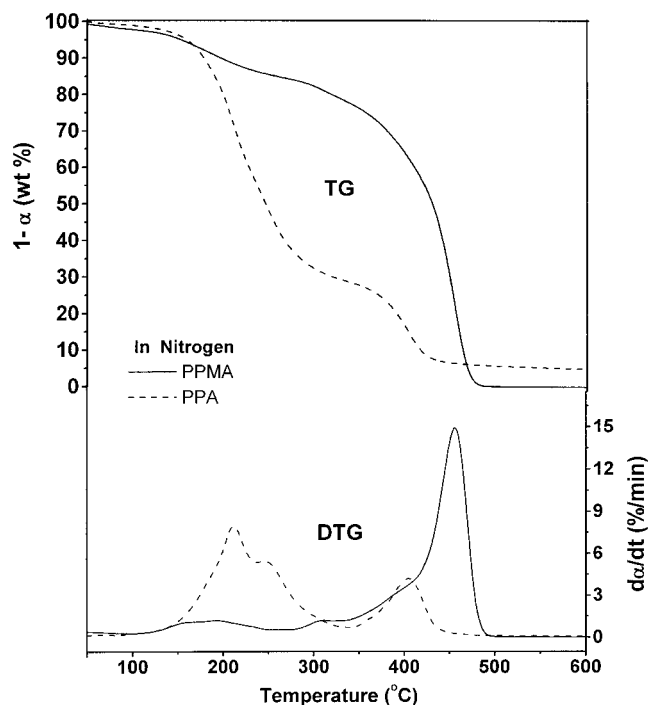


Figure 4 TG and DTG curves of the poly(*N*-phenyl methacrylamide) (—) and poly(*N*-phenyl acrylamide) (---) in flowing nitrogen at a heating rate of 10°C/min.

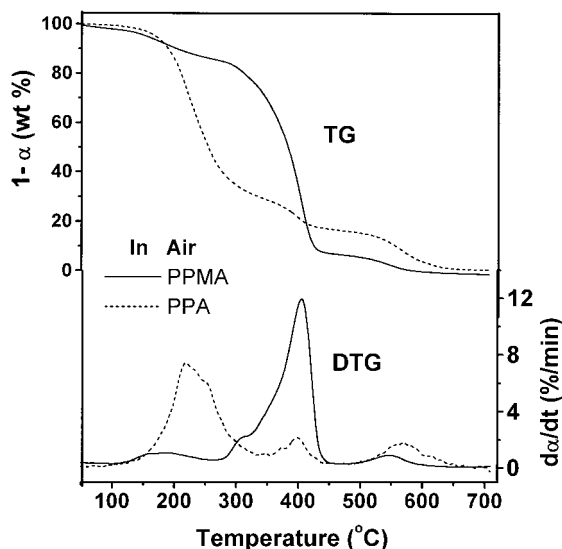


Figure 5 TG and DTG curves of the poly(*N*-phenyl methacrylamide) (—) and poly(*N*-phenyl acrylamide) (---) in flowing air at a heating rate of 10°C/min.

trapolation of the initial degradation portion of the TG curve. There is already significant weight loss at the temperatures higher than 140°C for PPMA and 180°C for PPA, indicating that both polymers exhibit low thermostability. In particular, at temperatures below 180°C, PPMA exhibits lower thermostability than that of PPA, possibly because of the relatively low molecular weight of PPMA and also the easy abstraction of methyl groups from the PPMA chain at relatively low temperatures, given that the single bond between the methyl group and the polymer backbone should be the weakest and sensitive to thermal attack. On the other hand, in a temperature range from 180 to around 450°C, PPMA exhibits much higher thermostability than that of PPA, perhaps because of the crosslinking stabilization resulting from the abstraction of methyl group from the PPMA chain at relatively low temperatures.

The thermal degradation behavior of both polymers varies slightly with the testing atmosphere. The thermal degradation of the PPA appears to occur through three major fast degradation steps in nitrogen but through two major fast degradation steps first and then two minor slow degradation steps in air, whereas

the PPMA exhibits two very minor slow degradation steps first and then one major fast degradation step in both atmospheres, and additionally very minor slow degradation step only in air, as shown in Table I.

Table I shows that the initial thermal degradation temperature T_d and two temperatures at the maximum weight-loss rate T_{dm1} and T_{dm2} for PPA are higher in air than in nitrogen, but a contrary situation for PPMA. Lower $(d\alpha/dt)_{m1}$ and $(d\alpha/dt)_{m3}$ but higher $(d\alpha/dt)_{m2}$ and char yield at 500°C for PPA and PPMA are found in air than in nitrogen. These results imply a higher thermostability for PPA in air than in nitrogen and slower degradation rate for PPMA in air than in nitrogen. The higher char value when the experiments are conducted in air rather than in nitrogen could be attributable to the stabilization of oxidation from the oxygen in the air. A similar higher char yield at 500°C in air than in nitrogen was observed for poly(4-vinylpyridine-*co*-divinylbenzene),⁶ although most of polymers exhibit higher char yields at elevated temperatures in inert atmospheres than in air.^{7,8} Note that higher degradation temperatures exhibited by PPA could be attributable to relatively high molecular weight and also larger sample size in air (2.9 mg) than in nitrogen (1.8 mg). An additional fourth degradation stage at 568 and 548°C for PPA and PPMA, respectively, must be attributed to the oxidative pyrolysis from the oxygen in air, leading to a complete combustion of residual char form at 400°C. Note that both PPA and PPMA, which have flexible aliphatic main chains, exhibit much lower thermal stability than that of thermotropic liquid crystalline copolyesters, which have rigid aromatic main chains.^{3,9}

Thermal degradation process

As listed in Table II, the temperature ranges of three-step decomposition in nitrogen and of four-step decomposition in air vary slightly with the change in testing atmosphere and in polymer from PPA to PPMA, indicating that their thermal processes are similar. The weight losses corresponding to three- or four-stage decomposition also vary slightly with testing atmosphere but vary significantly with changing polymer from PPA to PPMA. This variation in weight loss must be attributed to the molecular structural differ-

TABLE I
Thermal Degradation Characteristics of Poly(*N*-phenyl acrylamide) (PPA) and Poly(*N*-phenyl methacrylamide) (PPMA)

Polymer	Atmosphere	$T_d/T_{dm1}/T_{dm2}/T_{dm3}/T_{dm4}$ (°C)	$(d\alpha/dt)_m$ 1st/2nd/3rd/4th (% min ⁻¹)	Char yield at 500°C (wt %)
PPA	Nitrogen	180/214/247/407/—	8.2/5.4/4.3/—	5.3
PPA	Air	186/220/255/397/568	7.5/6.1/2.3/1.9	15.2
PPMA	Nitrogen	142/195/314/455/—	1.2/1.2/15.2/—	0
PPMA	Air	142/184/313/405/548	0.9/2.0/11.9/0.8	5.7

TABLE II
Temperature Range and Weight Loss of Each Degradation Step for the Poly(*N*-phenyl acrylamide) (PPA) and Poly(*N*-phenyl methacrylamide) (PPMA)

Polymer	Atmosphere	Temperature range (°C)				Weight loss (wt %)			
		1st step	2nd step	3rd step	4th step	1st	2nd	3rd	4th
PPA	Nitrogen	100–238	238–335	335–500	—	45.9	25.5	25.0	—
PPA	Air	100–242	242–340	340–470	470–700	44.4	26.2	13.4	16.0
PPMA	Nitrogen	100–258	258–342	342–500	—	15.6	7.1	77.3	—
PPMA	Air	100–266	266–325	325–470	470–620	14.7	8.7	70.4	6.2

ence. For example, PPMA contains an additional methyl group on each repeated unit as compared with PPA. The difference of molecular weight might be another reason. It appears that the PPA with relatively high molecular weight and wide molecular weight distribution loses weight faster in relatively low temperature ranges lower than 340°C, regardless of its relatively high T_d . The first-stage decomposition of PPA could correspond to the drastic pyrolysis of the polymer main chain and the subsequent second-, third-, and fourth-stage decompositions that correspond to the thermal and oxidative pyrolysis of residual char. On the contrary, the first- and second-stage decompositions of PPMA might correspond to the abstraction of the methyl group and subsequent crosslinking between the residual char. The third-stage decomposition of PPMA corresponds to major pyrolysis of the polymer's main chain. In conclusion, the multiple steps of the thermal degradation process of the polymers suggests the multiplicity of the macromolecular chain structures.

Thermal degradation kinetics

Two types of plots for the calculation of activation energy of the degradation of the PPA and PPMA are shown in Figures 6 and 7 by the Friedman and the Freeman–Carroll techniques, respectively.^{9–19} The calculated activation energy data are summarized in Table III. Apparently, the degradation activation energy and frequency factor for PPA are lower than those for PPMA in both atmospheres, although the decomposition order for PPA is higher than that for PPMA. The activation energy and frequency factor of the thermal degradation for PPA and PPMA are lower in air than in nitrogen. The activation energy and frequency factor values calculated by the Friedman technique are also lower than those by the Freeman–Carroll technique. As compared with the thermotropic liquid crystalline copolyesters having rigid aromatic main chains and then high thermal degradation temperature,⁹ the PPMA, especially the PPA, shows particularly low activation energy, frequency factor, and temperature of the first-step thermal degradation in both atmospheres. All of these indicate that both PPA and

PPMA exhibit low thermostability and decompose at a fast rate at relatively low temperatures because of their flexible aliphatic main chains.

CONCLUSIONS

The macromolecular structures of PPA and PPMA prepared by solution polymerization from *N*-phenyl acrylamide (PA) and *N*-phenyl methacrylamide (PMA) were investigated by FT-IR, ¹H-NMR, and GPC. Their thermal stability determined by TG method is lower and the degradation occurs in three stages in nitrogen and in four stages in air. The kinetic parameters of thermal decomposition of PPA and PPMA show a dependency of testing atmosphere and calculating technique, suggesting that the thermal degradation mechanism might vary with the atmosphere. PPA exhibits higher thermal degradation temperature but lower activation energy than those of PPMA. Both PPA and PPMA exhibit low thermostability and decompose rapidly at relatively low temperatures.

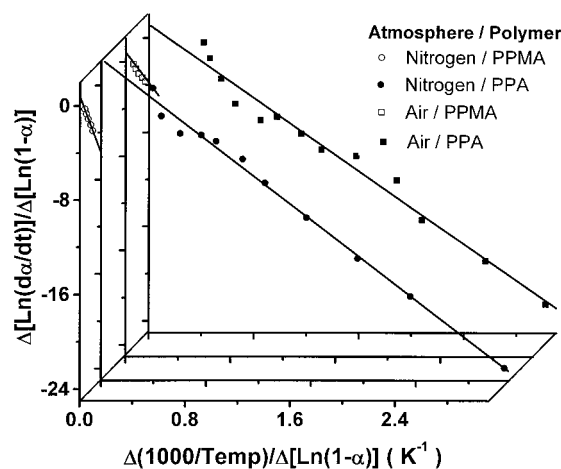
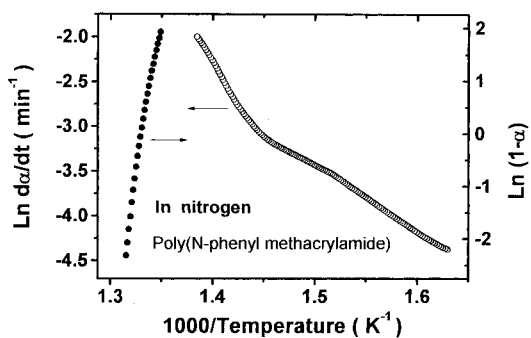
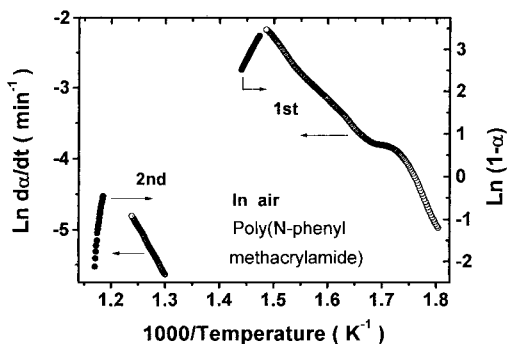


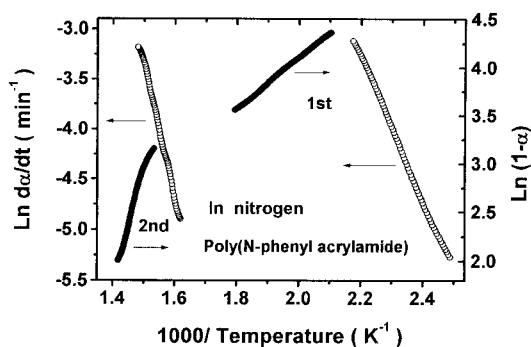
Figure 6 Application of the Freeman–Carroll method to the TG and DTG data obtained in nitrogen for poly(*N*-phenyl methacrylamide) (○) and for poly(*N*-phenyl acrylamide) (●), as well as in air for poly(*N*-phenyl methacrylamide) (□) and for poly(*N*-phenyl acrylamide) (■) for the calculation of activation energy of their major thermal decompositions.



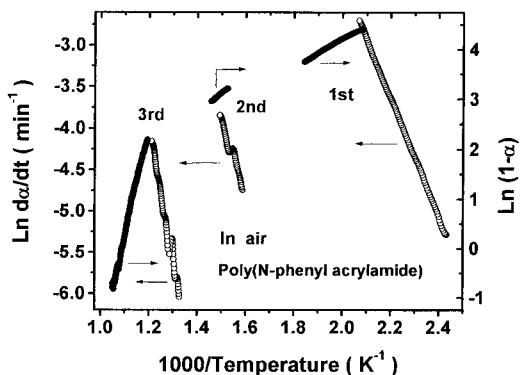
(a)



(b)



(c)



(d)

Figure 7 Application of the Friedman method to the TG and DTG data obtained for poly(*N*-phenyl methacrylamide) in nitrogen (a) and air (b) as well as poly(*N*-phenyl acrylamide) in nitrogen (c) and air (d) for the calculation of activation energy (○) and reaction order (●) of thermal decomposition.

TABLE III
Kinetic Parameters of the Thermal Degradation of Poly(*N*-phenyl acrylamide) (PPA) and Poly(*N*-phenyl methacrylamide) (PPMA)

Polymer	Atmosphere	Friedman technique		Freeman-Carroll technique	
		1st step $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)	3rd step $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)	4th step $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)	3rd step $E/n/\ln Z$ (kJ mol ⁻¹ /—/min ⁻¹)
PPA	Nitrogen	61/2.8/14	110/1.2/19	—	—
PPA	Air	59/2.6/13	71/2.2/12	133/1.6/19	71/2.2/16
PPMA	Nitrogen	—	64,161/0.2/25	—	249/0.8/40
PPMA	Air	136,70/0.4/14	115/0.2/19	—	133/0.7/23

References

1. Guo, W.; Mitchell, G. R. *Polymer* 1994, 35, 3706.
2. Fischer, H.; Poser, S.; Arnold, M. *Macromolecules* 1995, 28, 6957.
3. Li, X.-G.; Huang, M.-R. *Advanced Materials Engineering of Liquid Crystalline Polymers*; East China Normal University Press: Shanghai, China, 2000; pp. 404–412.
4. Hamouly, S. H.; Azab, M. M. *Polym Int* 1994, 34, 273.
5. Li, X.-G.; Huang, M.-R.; Shao, H.-T. *J Appl Polym Sci* 2002, 86, 1673.
6. Li, X.-G. *React Funct Polym* 1999, 42, 53.
7. Li, X.-G.; Huang, M.-R.; Bai, H.; Yang, Y.-L. *Macromol Mater Eng* 2001, 286, 421.
8. Li, X.-G.; Huang, M.-R.; Bai, H. *J Appl Polym Sci* 2002, 83, 1940.
9. Li, X.-G.; Huang, M.-R. *Polym Int* 1999, 48, 387.
10. Li, X.-G.; Huang, M.-R. *React Funct Polym* 1999, 42, 59.
11. Huang, M.-R.; Li, X.-G. *J Appl Polym Sci* 1998, 68, 293.
12. Huang, M.-R.; Li, X.-G.; Yang, Y.-L. *Polym Degrad Stab* 2001, 71, 31.
13. Li, X.-G.; Huang, M.-R.; Li, F.; Cai, W.-J.; Jin, Z.; Yang, Y.-L. *J Polym Sci Part A: Polym Chem* 2000, 38, 4407.
14. Li, X.-G.; Huang, M.-R.; Yang, Y.-L. *Polymer* 2001, 42, 4099.
15. Li, X.-G.; Huang, M.-R.; Yang, Y.-L. *Polym J* 2000, 32, 348.
16. Li, X.-G.; Duan, W.; Huang, M.-R.; Yang, Y.-L. *J Polym Sci Part A: Polym Chem* 2001 39, 3989.
17. Day, M.; Cooney, J. D.; Wiles, D. M. *J Appl Polym Sci* 1989, 38, 323.
18. Friedman, H. L. *J Polym Sci* 1964, C6, 183.
19. Freeman, E. S.; Carroll, B. *J Phys Chem* 1958, 62, 394.