# FAA Final Report

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## Summary of Completed Project

This final report includes four parts which have been completed during the period of time supported by this grant. The first part is thermal stability study of aromatic polyimides which synthesized at the University of Akron. The second part summaries the thermal stability and degradation mechanisms of high performance polyimide fibers produced at the University of Akron. The third part is the thermal degradation of PBZT, PBZO and Kevlar fibers. The fourth part is the publication list under the support of this grant.

## 1. Thermal degradation of aromatic polyimides

The choice of polyimide materials is based on the fact that this family of polymers not only possesses high thermal and thermo-oxidative stability, but also has a higher oxygen index and char yield than other polymeric materials such as phenolics, epoxies, polyesters and polyamides. A plot of oxygen index and char residue is shown in Figure 1. Our research focuses on the fire resistant properties of aromatic polyimide fibers, coatings and thermoplastics which have a specific molecular design and controlled architecture in order to achieve desired properties for applications in structural and interior components for aircrafts.

Both novel aromatic dianhydrides and diamines have been designed. Eight new dianhydrides of specific molecular architecture have been synthesized based on 2,2'-disubstituted 4,4',5,5'-biphenyltetracarboxylic dianhydrides (2,2'-disubstituted BPDAs). A series of twelve aromatic diamines, 4,4'-diamino-2,2'-disubstitutedbiphenyls, has also been synthesized. Polyimides made by these dianhydrides and diamines should exhibit high thermal and thermo-oxidative stability and high char yield.
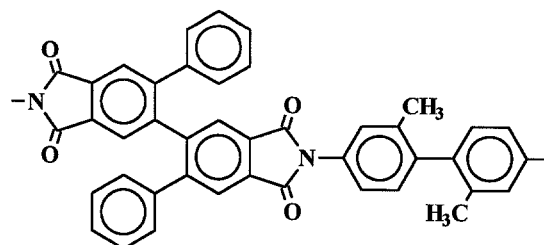
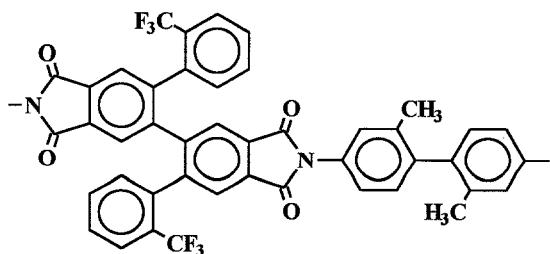The following aromatic polyimides have been synthesized (only the DMB series is listed)
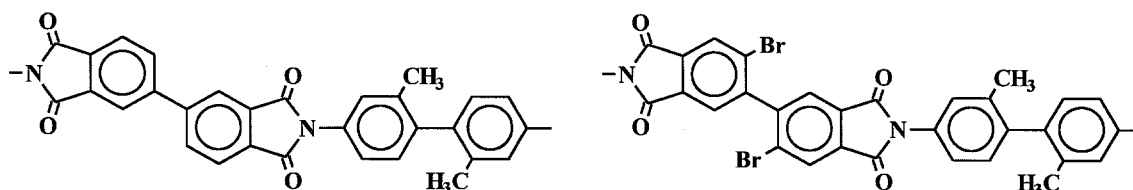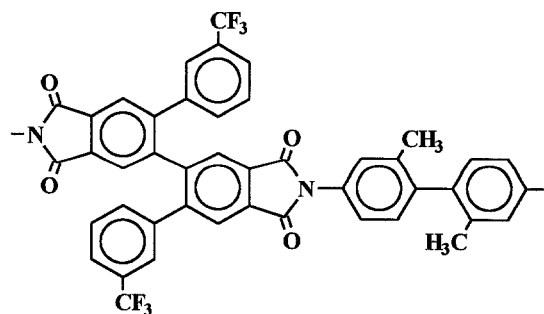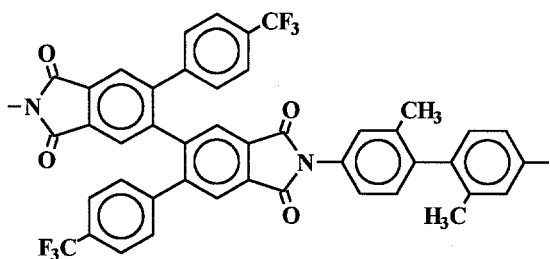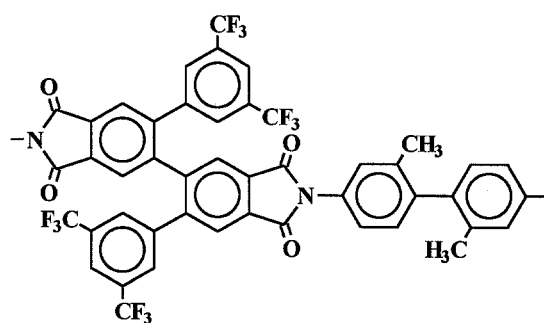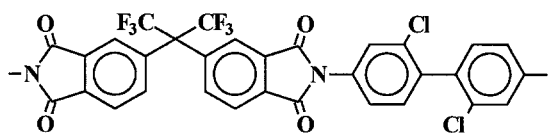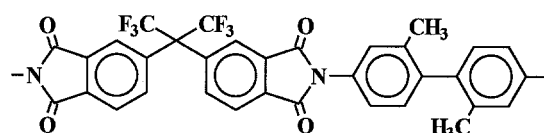
BPDA-DMB
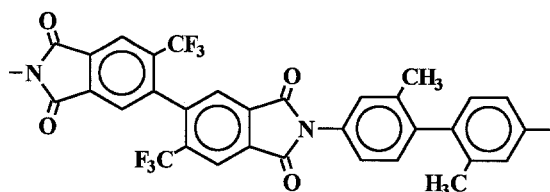
DBBPDA-DMB

HFBPDA-DMB

DPBPDA-DMB

O6FDPBPDA-DMB

O6FDPBPDA-DMB

P6FDPBPDA-DMB

M12FDPBPDA-DMB

6FDA-DCB
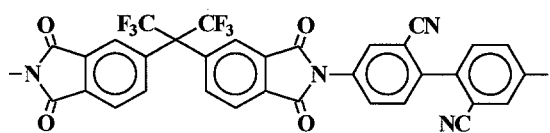
6FDA-DMB
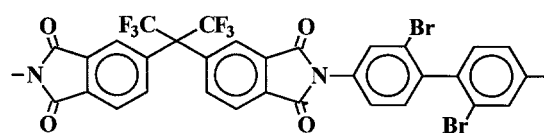
6FDA-DCN
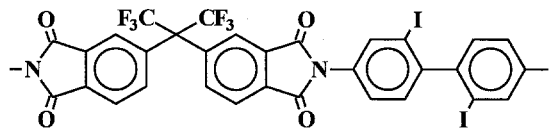
6FDA-DBB

6FDA-DIB

6FDA-PFMB

6FDA-MPPBZ

6FDA-P6FDPBZ

6FDA-O6FDPBZ

6FDA-M6FDPBZ

6FDA-M12FDPBZ

6FDA-3PBZ
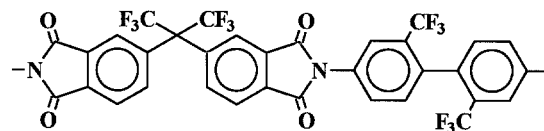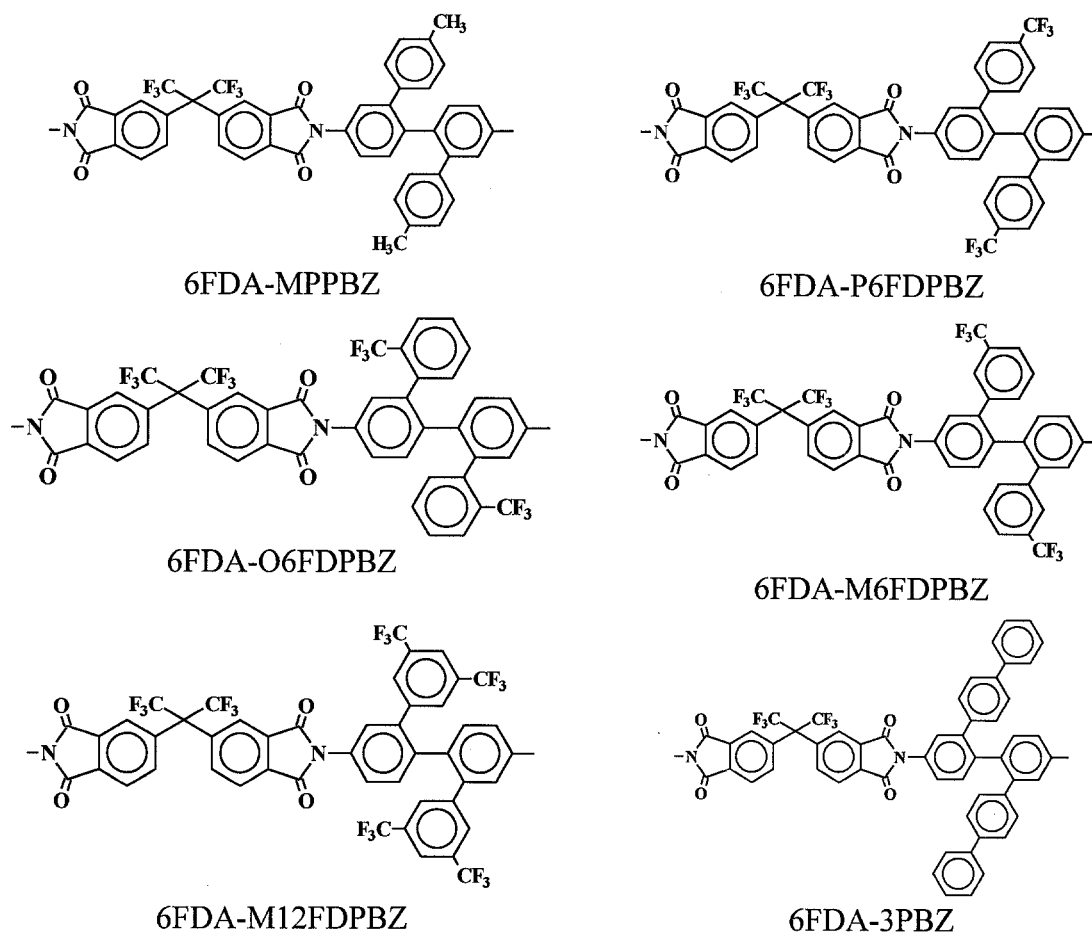
The thermal and thermo-oxidative stability has been examine using TGA in both dry nitrogen and air atmospheres. The results are listed in Tables 1 and 2.

Table 1. Temperatures for 2% and 5% weight loss in air and nitrogen for PFMB- and DMB-based polyimides with different dianhydrides
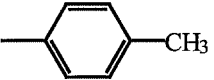
| Dianhydride | TGA (Air)* (°C) 2%/5%(wt) | TGA (N₂)* (°C) 2%/5%(wt) | TGA (Air)** (°C) 2%/5%(wt) | TGA (N₂)** (°C) 2%/5%(wt) |
|---|---|---|---|---|
| BPDA | 531/564 | 530/565 | 468/509 | 489/515 |
| DBBPDA | 486/518 | 492/523 | 412/441 | 437/458 |
| HFBPDA | 530/549 | 537/566 | 464/498 | 460/503 |

| | | | | |
|---|---|---|---|---|
| DPBPDA | 498/539 | 513/542 | 427/508 | 479/511 |
| O6FDPBPDA | 529/553 | 531/559 | 439/495 | 481/509 |
| M6FDPBPDA | 529/563 | 536/566 | 433/509 | 485/512 |
| P6FDPBPDA | 524/546 | 534/555 | 440/502 | 484/510 |
| M12FDPBPDA | 530/550 | 535/565 | 440/495 | 480/513 |
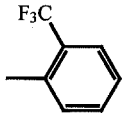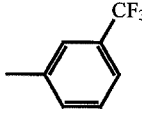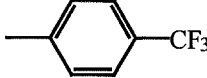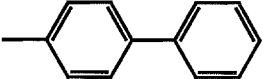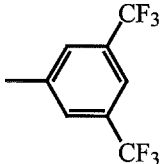
\* PFMB-based polyimides
\*\* DMB-based polyimides

Table 2.  Temperatures for 2% and 5% weight loss in air and nitrogen for 6FDA-based
polyimides with different diamines

| Diamine | 2,2'-Disubstituted Groups | TGA (Air) (°C) 2%/5%(wt) | TGA ($N_2$) (°C) 2%/5%(wt) |
|---|---|---|---|
| DCB | —Cl | 458/497 | 486/513 |
| DMB | —$CH_3$ | 480/503 | 488/505 |
| DCN | —CN | 475/513 | 500/528 |
| DBB | —Br | 434/472 | 457/504 |
| DIB | —I | 341/413 | 375/467 |
| PFMB | —$CF_3$ | 490/518 | 505/530 |
| MPPBZ | —⬡—$CH_3$ | 425/471 | 440/480 |

| | | | |
|---|---|---|---|
| O6FDPBZ | | 493/517 | 507/523 |
| M6FDPBZ | | 488/508 | 506/525 |
| P6FDPBZ | | 487/513 | 506/523 |
| 3PBZ | | 485/513 | 501/521 |
| M12FDPBZ | | 482/509 | 505/525 |

These polyimides were synthesized in refluxing *m*-cresol at high temperatures through a one-step route in which the intermediate poly(amic acid)s were not isolated. Most of the aromatic polyimides which we have synthesized can be easily dissolved in common organic solvents such as acetone, chloroform, 2-pentanone, cyclopentanone, methyl ethyl ketone, tetrahydrofuran, dimethylformamide, N-methylpyrrolidinone and dimethyl sulfoxide *etc.* and can be directly processed to form films or coatings. A major advantage of these aromatic polyimides is that they are extremely thermally and thermo-oxidatively stable. Due to their solubility, these polyimides possess excellent processibility and it is expected that they can be used as thin films or coatings on polymeric substrate surfaces as protective layers.

## 2. Thermal stability and degradation mechanisms of polyimide fibers

Two of the aromatic polyimides were chosen in our study, both of which are based on the synthesis of 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA) and 2,2'-disubstituted-4,4'-diaminobiphenyl (PFMB and DMB) using a one step route. These materials show excellent potential as fiber forming materials since their tensile properties are equivalent to or better than Kevlar fibers. In addition, these polyimides have two times higher compressive strengths than Kevlar, but more importantly, their thermal stabilities are at least 50°C to 100°C higher. The chemical structure of BPDA-PFMB is:
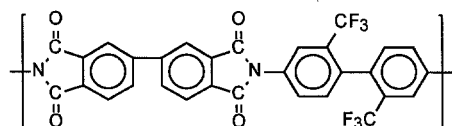
and BPDA-DMB is
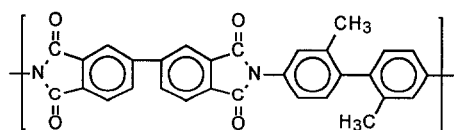
Thermal degradation can be roughly examined *via* nonisothermal thermogravimetric (TG) experiments under dry nitrogen and air. Both polyimides exhibit excellent thermal and thermo-oxidative stability. The 5% weight loss temperature of these materials are above 500°C for BPDA-DMB and close to 600°C for BPDA-PFMB. However, these type of experiments do not reflect their true thermal degradation routes. A more precise measurement requires study of the thermal degradation kinetics, which are carried out under isothermal conditions. Only 1% weight loss is detected at 460°C after 5 hours, indicating the excellent thermal stability of BPDA-PFMB in nitrogen. However, in air, the 1% weight loss is observed at 400°C after 5 hours. This difference of 60°C reveals an effect of thermo-oxidation. Based on the kinetics model, activation energies of BPDA-PFMB can be calculated using the following equation:

$$ln(t) = lng(\alpha) - lnA + E_a/(RT) \tag{1}$$

where $t$ is the isothermal time, $g(\alpha)$ is the integral of the rate of weight loss, $A$ is the pre-exponential factor, $R$ is the gas constant and $E_a$ is the thermal degradation activation energy. The slope of a plot between $ln(t)$ and $1/T$ at constant weight fraction loss $(\alpha)$ yields this activation energy. This experimental procedure can also applied to BPDA-DMB and other materials such as PBO, PBZT and Kevlar. Their thermal degradation activation energies in both dry nitrogen and air are listed in Table 3.

**Table 3.** Thermal degradation activation energies for different polymeric materials

| Materials | $E_a$ in dry nitrogen (kJ/mol) | $E_a$ in air (kJ/mol) |
|-----------|-------------------------------|----------------------|
| BPDA-PFMB | 300 | 200 |
| BPDA-DMB | 200 | 135 |
| PBO | --- | 130 |
| PBZT | --- | 115 |
| Kevlar | --- | 100 |

In order to learn about the detailed thermal degradation mechanism, TG-mass spectroscopy (TG-MS) was used at a heating rate of 3°C/min. The temperature dependence of the total ionization current is shown in Figures 6 and 7. The maxima arise from the release of six major fragments: CO, HCN, $NH_3$, HF, $COF_2$ and $HCF_3$ arising from thermal cracking of the diimide and pendant loss. The overall profile indicates that the maximum rate of thermal

degradation under vacuum occurs at around 595°C. The results illustrate that the degradation of the pendant groups has maximum intensity at 580°C, as indicated by the $HCF_3$ ion. The thermal stability of the pendant trifluoromethyl groups is of paramount importance. The electron withdrawing nature of the pendant groups in the 2,2'-position of the diamines is responsible for stabilizing the polymer. At higher temperatures, we observe the main chain degradation products through the HCN and $NH_3$ ions. We are currently carrying out the TG-MS experiments on other polyimides and polymers in order to compare the degradation mechanisms.

## 3. Thermal stability examination of high performance fibers

Mechanical property measurements on BPDA-PFMB and BPDA-DMB fibers show a tensile strength of 3.2 GPa and a modulus of 130 GPa. These two newly developed polyimide fibers have been selected for evaluation and comparison of their thermo-oxidative stabilities with PBO, PBZT and Kevlar 49 fibers.

 PBO

 PBZT

 Kevlar
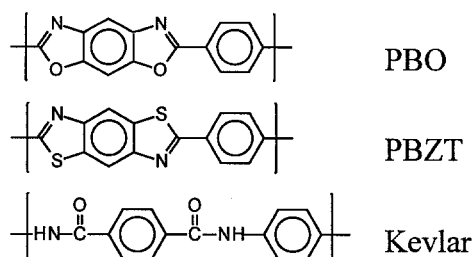
These five fibers have been isothermally aged under circulating air at 205°C. The tensile strength, elongation and modulus have been monitored at different aging times of 100, 250, 500, 750, 1000, 1500, 2000 and 2500 hours, respectively.

The most reliable information on the real thermo-oxidative stability of a fiber can be obtained from the study of changes in its physical, and in particular, mechanical properties upon prolonged isothermal aging times at elevated temperatures. Study of the changes in tensile strengths of BPDA-PFMB, BPDA-DMB, PBO, PBZT and Kevlar 49 fibers after aging for different times in circulating air at 205°C shows that the tensile strength of the BPDA-PFMB fiber remained constant during the first 100 hour exposure and the strain of the fiber decreased about 12%. Thus, the modulus remained unchanged. This phenomenon is similar to the case of annealing a fiber at constant length. In this annealing process, the tensile strength and modulus of the fibers increase and elongation decreases, indicating that further development of crystallinity and orientation in BPDA-PFMB fibers is achieved. Similarly, the tensile strength of BPDA-DMB fibers were unchanged in the first 100 hour exposure. In contrast, it is evident that the strength retention of PBO, PBZT and Kevlar 49 fibers drop by 5%, 6% and 10%, respectively for the same aging time.

During the isothermal aging process, the strength retention *versus* aging time can be divided into three stages as shown in Figure 8, *i.e.* 0-250 hours, 250-1000 hours and 1000-2500 hours. Table 4 lists the rates of changing strength retention with respect to time. For PBO, PBZT and Kevlar 49 fibers, their strength retention decrease rapidly in the first stage. The rate of decline slows in the second stage, and decreases further in the third stage. Quantitatively, the

rates of strength retention change in the first stage are almost twice as fast as those in the second stage; similarly, in the second stage, the changes are also twice as fast as those in the third stage. Surprisingly, for BPDA-DMB fibers, it was found that the smallest strength retention change is in the first stage. However, the changes in the second and third stages are similar to the cases of PBO, PBZT, Kevlar fibers. Finally, for BPDA-PFMB fibers, no decrease of strength was found in any of the three stages.

After 2500 hours of aging at 205°C, the strength retention changes of BPDA-PFMB, BPDA-DMB, PBO, PBZT, Kevlar fibers are 100%, 66%, 61%, 50%, and 39%, respectively. This fits well with the thermal degradation activation energies calculated from TG experiments (Table 3). It is important to note that the difference between the two $CF_3$ groups in the diamine in BPDA-PFMB as compared to the two $CH_3$ groups in the BPDA-DMB diamine contributes to the difference in the thermo-oxidative stabilities of these materials. This may again be attributed to the electron withdrawing nature of the $CF_3$ *versus* the electron donating tendency of the $CH_3$ group.

The strain retention changes of five fibers with respect to the isothermal aging time in circulating air show that the strain retention tendency is the same as that of the strength retention for these fibers. It is surprising that the strain retention of PBO fibers shows a drastic decrease in the first 100 hours of aging. Further research is necessary to investigate the cause of this phenomenon. For BPDA-PFMB fibers, the strain on the fiber decreases in the first 100 hours of aging, while the strength increases slightly, and as a result, the modulus increases. In general, the change of modulus during the isothermal aging is critically dependent upon the relative changes between the strength and strain.

During isothermal aging in air, it is speculated that molecular mechanisms may yield macroscopic changes in mechanical properties of the fibers, in particular, the tensile properties. These mechanisms may include scission of polymer chains, completion of cyclization, and crosslinking in chemical reactions, as well as crystallization, crystal perfection and orientation changes in physical reactions. The main effect may be the scission of the macromolecules as a result of thermal degradation. With increasing isothermal aging time, the color of the fibers are drastically changed (except for the polyimide fibers), which is believed to be caused by oxidation. Finally, although PBO fibers do not show the best thermo-oxidatitive stability, they still retain the best tensile strength even after long-term isothermal aging.

**Table 4.** Reduction in Fiber Strength with Different Isothermal Stages of Aging Time in Air at 205°C

| Sample | First Stage 0-250 hr(%) | Decreasing Rate (%/hr) | Second Stage 250-1000 hr(%) | Decreasing Rate (%/hr) | Third Stage 1000-2500 hr(%) | Decreasing Rate (%/hr) |
|---|---|---|---|---|---|---|
| BPDA-PFMB | 0 | 0 | 0 | 0 | 0 | 0 |
| BPDA-DMB | 1 | 0.004 | 17 | 0.022 | 17 | 0.011 |
| PBO | 11 | 0.044 | 15 | 0.020 | 13 | 0.009 |
| PBZT | 12 | 0.048 | 19 | 0.025 | 19 | 0.013 |
| Kevlar 49 | 17 | 0.068 | 23 | 0.031 | 21 | 0.014 |

## 4. Publications under this support

1.      Fuming Li, Liyan Huang, Yi Shi, Xigao Jin, Zongquan Wu, Zhihao Shen, Cathy Chung, Richard E. Lyon, Frank W. Harris and Stephen Z. D. Cheng, Thermal Degradation Mechanism and Thermal Mechanical Properties of Two High Performance Aromatic Polyimide Fibers. *Journal of Macromolecular Science, Physics,* B38, 107-122, **1999**.

2.      Fuming Li, Xing Fang, Chi-Chian Chen, Frank W. Harris, and Stephen Z. D. Cheng, Diamine Architecture Effects on Glass Transitions, Relaxation Processes and Other Material Properties in Organo-Soluble Aromatic Polyimide Films. *Polymer,* 40, 4571-4583, **1999**.

3.      Fuming Li, Jason J. Ge, Paul S. Honigfort, Xing Feng, Jyh-Chien Chen, Frank W. Harris and Stephen Z. D. Cheng, Dianhydride Architecture Effects on Thermal, Optical Properties and Relaxation Behaviors in Organo-Soluble Aromatic Polyimide Films. *Polymer*, 40, 4987-5002, **1999**.

4.      Zongquan Wu, Fuming Li, Liyan Huang, Yi Shi, Xigao Jin, Xing Fang, Kathy Chuang, Richard E. Lyon, Frank W. Harris and Stephen Z. D. Cheng, The Thermal Degradation Mechanism and Thermal Mechanical Properties of Two High Performance Heterocyclic Polymer Fibers. *Journal of Thermal Analysis*, 59, 361-373, **2000**.