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Relative Thermophysical Properties of Some Polyimidazopyrrolones

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Relative Thermophysical Properties of Some Polyimidazopyrrolones

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SUMMARY

A comparative thermogravimetric study of eight polyimidazopyrrolone films of varying composition revealed that the thermal stability of the polymers increased with increasing theoretical percentages of carbonyl groups within the polymer repeat unit. The films degraded more rapidly in air than in vacuo, but the order of stability was the same in the two environments. Dynamic heating of the film in vacuo developed three distinct temperature regions in which maximum rates of weight loss occurred at characteristic temperatures, and each temperature region was associated with the evolution of a particular gaseous species.

INTRODUCTION

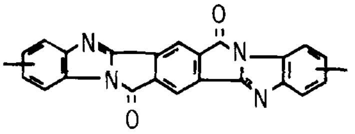
In an attempt to relate chemical structure with changes occurring during thermal and oxidative degradation of some aromatic/heterocyclic polymers, a series of thermogravimetric analyses was conducted to provide comparisons among thermal stabilities of eight polyimidazopyrrolone (pyrrone) films. The eight polymers studied were formed from two different dianhydrides and four different tetraamines and were heated at a constant heating rate (1°C/min) in air and in vacuo. Infrared spectra and mass spectrographic analysis of the evolved gases were used to supplement the thermograms in relating polymer structure to thermal behavior.

EXPERIMENTAL

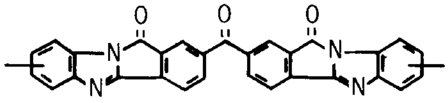
The pyrrones were prepared using pyromellitic dianhydride (PMDA) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) [1-3]. Each dianhydride was polymerized with four different tetraamines: 3,3′-diaminobenzidine (DAB), 3,3′,4,4′-tetraaminodiphenyl ether (TADPO), 3,3′,4,4′-tetraaminodiphenylmethane (TADPM), and 3,3′,4,4′-tetraaminobenzophenone (TABP).

The theoretical polymer repeat units and their abbreviations are shown in Table 1. For comparative purposes a polybenzimidazole, designated PBI-I-DAB, was prepared from diphenyl isophthalate and 3,3′-diaminobenzidine; a polyimide, which was prepared from PMDA and oxydianiline, was abbreviated as PMDA-ODA.

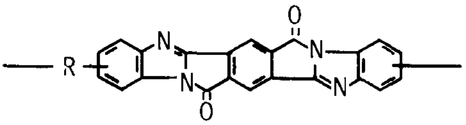
Table 1. Polyimidazopyrrolone Repeat Units



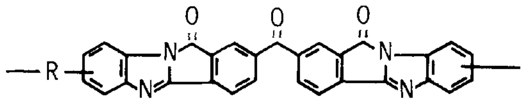
PMDA-DAB



BTDA-DAB



R = -O- : PMDA-TADPO
R = -CH$_2$- : PMDA-TADPM
R = -CO- : PMDA-TABP



R = -O- : BTDA-TADPO
R = -CH$_2$- : BTDA-TADPM
R = -CO- : BTDA-TABP

Films were formed by casting polymer solutions onto glass plates and drying them in a forced-airflow oven at 125°C for 1 hr. The films were stripped from the plates and postcured in air at 300°C for 2 hr. Weight-loss specimens 0.635 cm in diam, with nominal thickness of 0.0025 cm and initial weights of 2.05 ± 0.03 mg, were die-cut from the films. Separate specimens 0.00025-0.00050 cm (0.1-0.2 mil) thick were used for the infrared study.

The thermogravimetric apparatus used for measuring the thermal stability in vacuo was an all metal-glass system [4]. Ion pumps maintained the complete system at 10^{-6} Torr or less at all times. The main components were (1) a Cahn RG electrobalance, (2) quartz suspension fibers, (3) 3/8-in.-o.d. by 1/8-in.-high platinum sample pan, (4) chromel-alumel thermocouples within the vacuum chamber, (5) a 2-in.-diam by 12-in.-long furnace with adjustable tapping, and (6) a magnetic deflection-type mass spectrometer. A separate electrobalance system similarly arranged was used for tests made in air. Infrared scans were obtained with a Perkin-Elmer 421 spectrophotometer.

The initial weight was taken as the weight of the sample after it had been preconditioned at 100°C for 30 min to eliminate absorbed moisture. The temperature was increased 1°C/min until sample pyrolysis was complete or until 800°C was reached.

Residual gas measurements were obtained at 10°C intervals over the 2-100 mass range, with emphasis placed upon peaks from mass 2 to 50. Spectra were recorded from 1×10^{-8} Torr, denoting background pressure. For each spectrum individual partial pressures additively accounted for no less than 90% and no more than 100% of the observed total pressure.

RESULTS

Figure 1 compares the behavior in air of one of the polymers, PMDA-TABP, with its behavior in vacuo. It can be seen that rapid oxidation begins at about 450°C, while thermal degradation in vacuo does not begin until about 480°C, and the slope of the in vacuo curve is much less precipitous. The difference in behavior in the two environments evidenced by PMDA-TABP is typical of all the polymers. In the following discussion, the onset of rapid weight loss was considered as the criterion for the loss of stability.

Figure 2 compares polymers prepared from a common dianhydride (PMDA) but with four different tetraamines, and Fig. 3 presents similar results for a series in which the common dianhydride is BTDA. The relative order of oxidative stability was the same for polymers from both dianhydrides, with the TABP tetraamine imparting the greatest resistance to oxidation followed by the DAB, TADPM, and TADPO films. Figure 4 presents thermograms for the four BTDA-type films heated in vacuo. With respect to the onset of rapid weight losses between 490 and 475°C, it is observed that the polymers follow the same order of stability in the two environments.

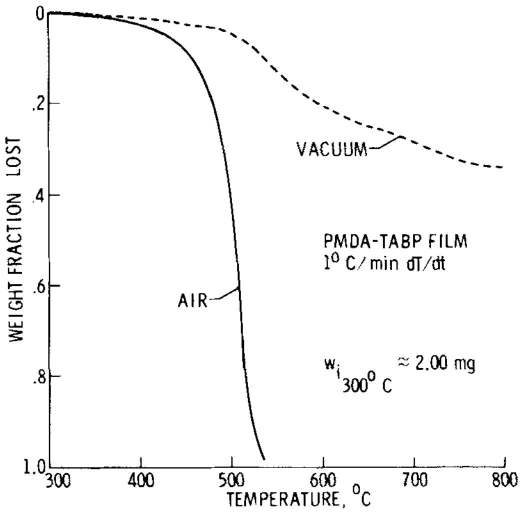


Fig. 1. Thermograms of PMDA-TABP heated in air and in vacuo.

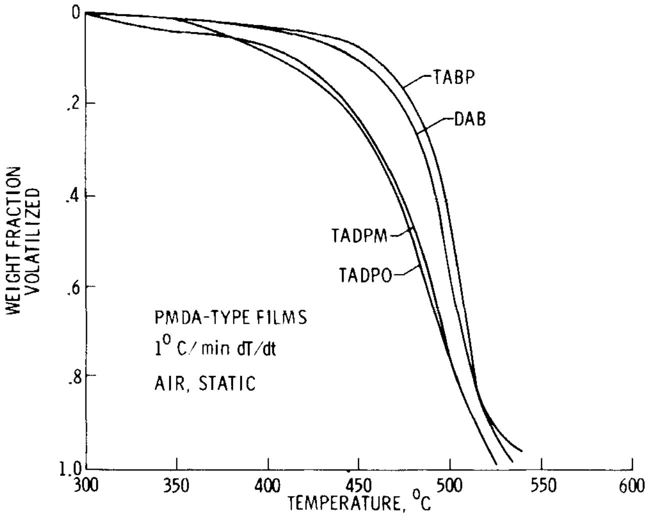


Fig. 2. Thermograms in air of pyrrone films prepared from pyromellitic dianhydride.

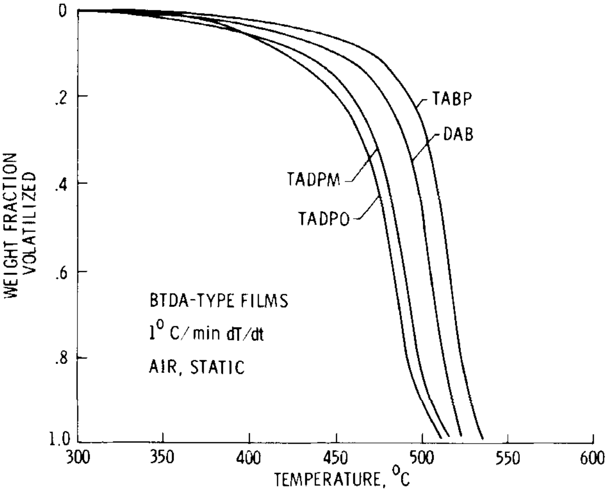


Fig. 3. Thermograms in air of pyrrone films prepared from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride.

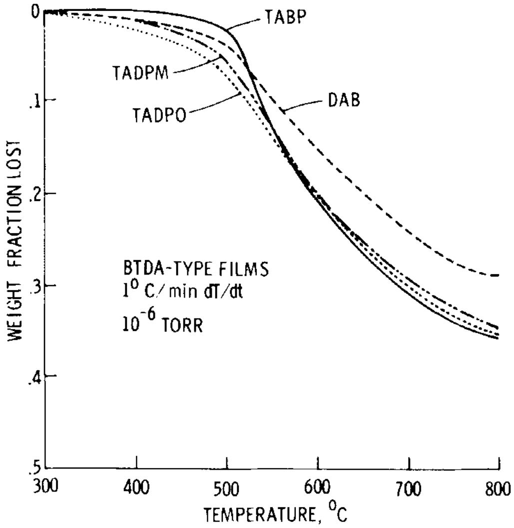


Fig. 4. Thermograms in vacuo of pyrrone films prepared from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride.

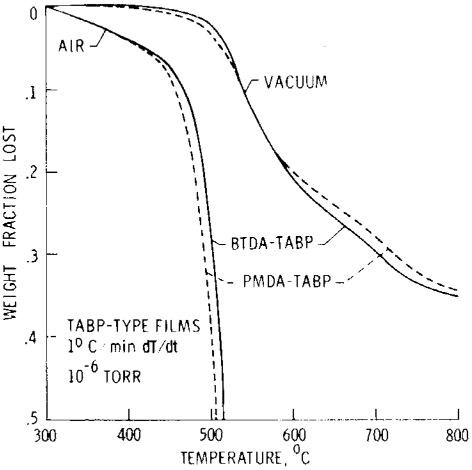


Fig. 5. Effect of dianhydride structure on thermal stability of TABP pyrrone films.

A comparison of polymers prepared from a common tetraamine but with different dianhydrides indicates that the BTDA imparts slightly more resistance to degradation in air and in vacuo than does PMDA, regardless of the tetraamine used. Figure 5 shows the typical effect of changing the dianhydride structure on thermal stability.

Attempts to correlate observed relative thermal stability with elemental composition and structural features (see Table 2) resulted in only one meaningful parameter, namely, thermal stability increased with increasing total carbonyl content, which varies from 14.9 to 22.8%. Also, the positions of these carbonyls within each repeat unit varies from one polymer system to another. The more thermally stable polymide, PMDA-ODA, which has the highest carbonyl content of any polymer listed in the table, was included for comparison.

Infrared spectra (Fig. 6) of nominal 0.1-mil-thick pyrrone films cured at 300°C in air for 1 hr showed progressive changes in band frequencies and relative band intensities in the 1700-1800 cm^{-1} region, indicating increasing imide content. Increasing imide content appears to parallel the increase in carbonyl content calculated from the theoretical repeating unit (see Table 2).

In Fig. 6, infrared band developments in regions of interest are shown for five of the pyrrone films, along with typical imide absorption provided by the PMDA-ODA polyimide, and imidazopyrrolone formation provided

Table 2. Molecular Weight Percentages of Elements and Groups Occurring in the Theoretical Unit Structure of Eight Polyimidazopyrrolones

Polymer	Molecular weight	C	H	N	O	CO
BTDA-TABP	492	73.2	2.4	11.4	13.0	22.8
BTDA-DAB	464	75.0	2.6	12.4	10.4	18.1
BTDA-TADPM	478	75.3	2.9	11.7	10.0	17.6
BTDA-TADPO	480	72.5	2.5	11.7	13.3	17.5
PMDA-TABP	388	71.2	2.1	14.4	12.4	21.7
PMDA-DAB	360	73.4	2.2	15.6	8.9	15.6
PMDA-TADPM	374	73.8	2.7	15.0	8.6	15.0
PMDA-TADPO	376	70.2	2.1	14.9	12.8	14.9
PMDA-ODA[a]	382	69.1	2.6	7.3	20.9	29.3

[a] A polyimide based on oxydianiline.

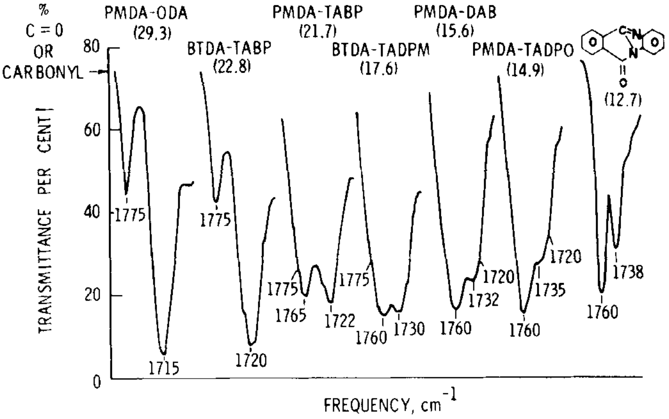


Fig. 6. Effect of structure on infrared spectra.

by the model compound, benzoylenebenzimidazole. PMDA-TADPO, the least thermally stable film, developed a dominant 1760 cm^{-1} band and a secondary 1735 cm^{-1} band, and did not exhibit any shoulder at 1775 cm^{-1}. BTDA-TABP, the most thermally stable pyrrone film, developed a sharp definite band at 1775 cm^{-1} and a broad, deep 1720 cm^{-1} band, suggesting that a high degree of imide character was attained.

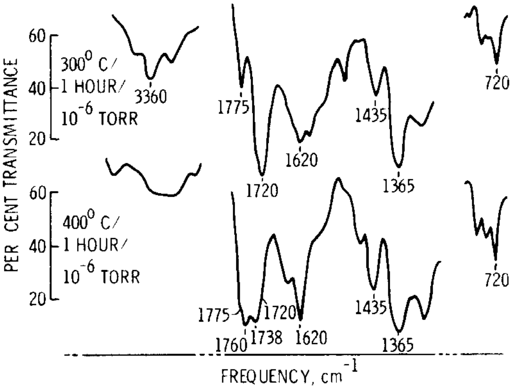


Fig. 7. Infrared spectra of BTDA-TABP films approximately 0.4-mil thick.

Figure 7 presents portions of infrared spectra from BTDA-TABP film which was heated in vacuo for 1 hr at 300 and 400°C. Absorption bands assigned to pyrrone carbonyl vibrations developed at 1760 and 1738 cm^{-1} upon heating at the higher temperature. The development of a 1620 cm^{-1} absorption band assigned to the C=N stretch and the reduction in intensity of the 1720 cm^{-1} imide carbonyl band, together with the loss of bands in the 3200-3600 cm^{-1} region, support the proposed reaction of amine and imide groups to form the imidazopyrrolone structure. In spite of this evidence of the formation of some pyrrone structure when the BTDA-TABP film is heated to 400°C, the continued presence of a 1775 cm^{-1} shoulder points to the retention of some isolated imide structure.

Each polymer developed three distinct regions of weight loss when heated under vacuum (Fig. 8). The maximum rates of weight loss occurred at characteristic temperatures with the evolution of relatively simple gaseous species. In the first region, I, centered at approximately 390°C, water was the major constituent evolved, suggesting additional polymer cyclization which was not completed by the previous curing at 300°C. Infrared samples progressively heated to 400°C showed increasing definition of the "imidazole" (C=N) band at 1620 cm^{-1}, primarily due to loss of neighboring bands presumably associated with unreacted amine groups.

During the second period, II, of major weight loss (500-600°C), carbon monoxide was the dominant gas detected, along with lesser amounts of carbon dioxide, water, and ammonia. The partial pressure of carbon monoxide evolved for each of the eight pyrrone structures

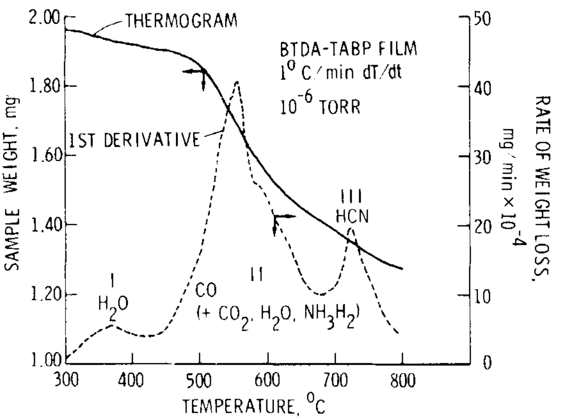


Fig. 8. Thermogram and its first derivative for BTDA-TABP film heated in vacuo at 1°C/min.

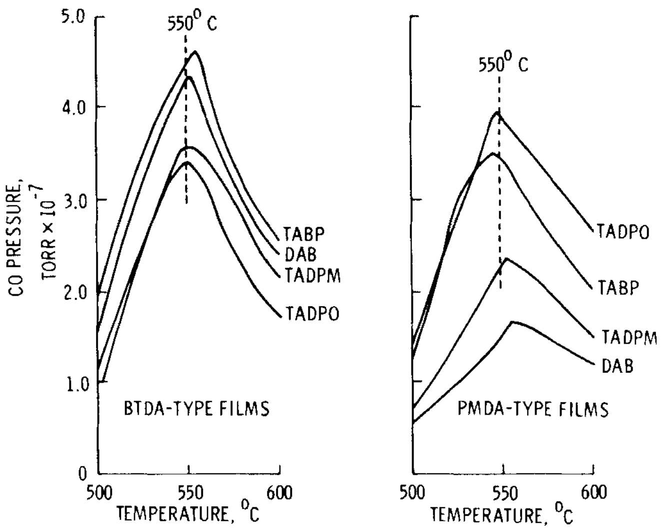


Fig. 9. Partial pressure of carbon monoxide from pyrolysis of pyrrone films.

is plotted versus increasing temperature in Fig. 9. In each case, CO pressure maximized at 550 ± 5°C, denoting only slight variation in energy required to split out the carbonyl moiety, which indicates a strong degree of structural similarity among the eight polyimidazopyrrolones. Infrared spectra of films heated above 480°C showed progressive disappearance of bands assigned to imide and pyrrolone carbonyl groups, with retention of bands assigned to benzimidazole structure. Above 550°C, the pyrrone spectra increasingly resembled spectra obtained from the polybenzimidazole film (PBI-I-DAB).

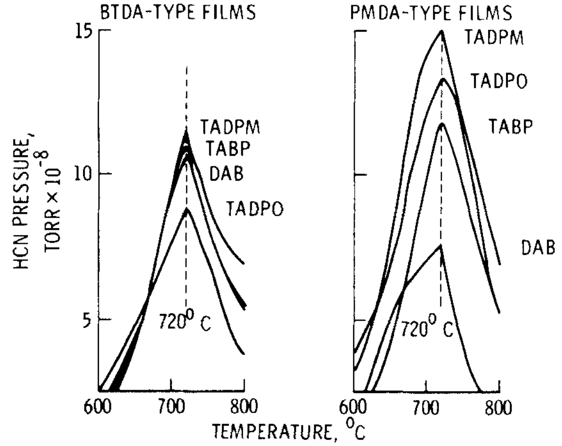


Fig. 10. Partial pressure of HCN from pyrolysis of pyrrone films.

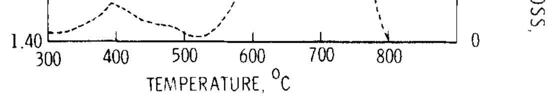


Fig. 11. Thermogram in vacuo of PBI-I-DAB film.

The third region of weight loss, III, centered at 720 ± 10°C, was characterized by the evolution of mass 27, assumed to be hydrogen cyanide (Fig. 10). For the PBI-I-DAB films, the highest rate of weight loss also occurred at 720°C, as shown in Fig. 11, and again mass 27 was dominant. Similar results have been reported for related PBI materials [5]. Pyrrones, when heated at 1°C/min in vacuo, manifest 1) a maximum conversion temperature near 400°C and 2) subsequently, a relatively early loss of imide character coupled with an apparent drive toward a benzimidazole structure.

At 800°C in vacuo, thermograms tended to develop plateaus where weight losses ranged between 25 and 35%. The percentage of carbon within the benzenoid portion of a pyrrone might be a regulating factor at this temperature. For example, the theoretical percentages of benzenoid carbon in BTDA-TABP and PMDA-TABP are 58.4 and 55.7, respectively. This suggests that a well-cured BTDA-TABP in vacuo should retain a greater portion of its weight at 800°C than PMDA-TABP. However, this is not the case, as seen in Fig. 5 where the more stable BTDA-TABP film loses more weight than PMDA-TABP at 800°C. The difference in weight loss occurs primarily around 600°C, which corresponds to evolution of CO and CO_2. The BTDA-TABP film with the higher theoretical carbonyl content (22.8% vs. 21.7%) has more CO available to lose. Further consideration of this type of weight loss leads to a comparison of the behavior of films from closely related diamines and tetraamines. The polyimide, PMDA-ODA, should contain two more CO groups per repeat unit than the polyimidazopyrrolone, PMDA-TADPO. These two additional CO groups represent 14.7% of the PMDA-ODA unit molecular weight. As shown in Fig. 12, the polyimide has superior relative thermal stability in vacuo up to 570°C but undergoes a 14.9% greater weight loss at 800°C.

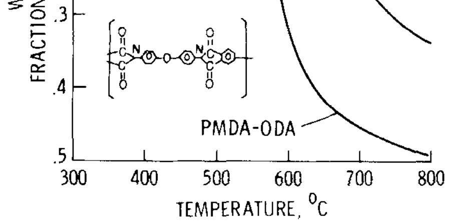


Fig. 12. Thermograms in vacuo for a polyimide and a polyimidazopyrrolone with related amines.

CONCLUSIONS

These results provide: 1) A distinctive pattern of thermal degradation for the eight pyrrone films, 2) strong indications that relative thermal stability of a polyimidazopyrrolone is primarily related to the carbonyl content of the polymer repeat unit, and 3) evidence that polyimidazopyrrolones, when heated beyond 550°C in vacuo, exhibit a pattern of thermal degradation which appears similar to that noted for polybenzimidazoles.

ACKNOWLEDGMENTS

The author is indebted to Dr. Vernon L. Bell for providing the polymer samples and for his detailed discussions concerning their preparation and chemistry. Special thanks are due Mr. Harold D. Burks for the infrared spectral measurements, Mr. Philip R. Young for his use of unpublished model compound data, and Dr. Norman J. Johnston for his analyses of the infrared spectra.

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Discussion of Paper by Robert A. Jewell

Relative Thermophysical Properties of Some Polyimidazopyrrolones

W. Wrasidlo: In recording infrared spectra of films for various pyrrones, to what extent could you control the sample concentration? Is it possible that the differences of carbonyl absorption for various films are due to experimental errors?

R. Jewell: No, for each of eight pyrrone films similarly converted, it is the progressive shifting of frequencies assigned to carboxyl absorption bands that is studied, rather than changes in band intensities.

H. Levine: 1) Your work is interesting and significant because it shows an inherent danger in model compound work. Such work shows pyrrone goes by way of amine imide with exclusion of carboxy benzimidazole. Your data definitely show this to be incorrect for polymer formation. Further, presence of benzimidazole accounts for lesser stability of pyrrone film compared with pure polyimide. 2) You should recalculate the correlation of C=O content to stability because your work neglected to take into account differences in Mer weights.

R. Jewell: 1) This study infers that pyrrone converts by way of both imide amine and carboxy benzimidazole, and that with increasing carbonyl content, conversion through imide amine is increased. Our model compound work, as yet unpublished, suggests this dual routing. 2) Carbonyl contents were based upon molecular weight of polymer repeat unit structure and reported as percentages.