Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

DETERMINATION OF THE AMOUNT OF ASSOCIATED SOLVENTS IN POLY(AMIC ACID)S BY THERMOGRAVIMETRY*

C. W. Tsimpris and K. G. Mayhan

Department of Chemical Engineering and the Graduate Center for Materials Research, University of Missouri–Rolla, Rolla, Missouri 65401 (U. S. A.)

(Received April 8th, 1971; in revised form May 17th, 1971)

ABSTRACT

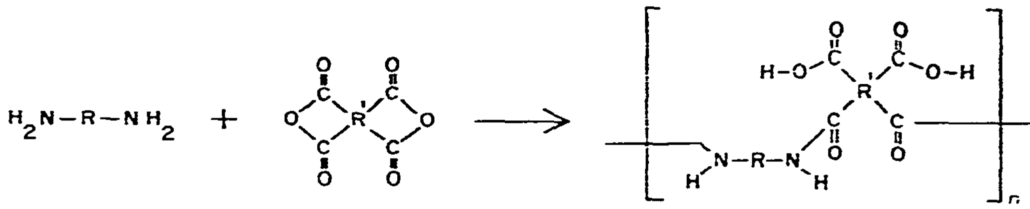
A method is presented by which thermogravimetry can be used to determine the amount of associated solvent in samples of solid poly(amic acid)s. Results are confirmed by IR and mass spectrometry and by experimental weight loss measurements.

INTRODUCTION

The methods for the determination of polymer molecular weights require that the concentrations of polymer solutions be accurately known. In the synthesis and recovery of poly(amic acid) prepolymers for polyimides, solvent molecules are associated with the polymer molecules making concentration determination difficult. A method has been developed to determine the amount of solvent present in a sample of a solid poly(amic acid) by means of thermogravimetry.

EXPERIMENTAL

Poly(amic acid)s were synthesized by methods similar to those described in the literature[1–6]. Poly(amic acid)s are prepared by reacting a diamine and a dianhydride in a suitable solvent as shown in Eqn. 1.



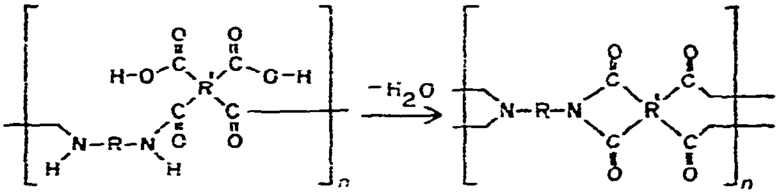
(1)

The poly(amic acid) can then be converted to the polyimide by heat or by chemical means as shown in Eqn. 2.

---

*Contribution No. 119 of the Graduate Center for Materials Research, University of Missouri–Rolla.

Thermochim. Acta, 3 (1971) 125–132


(2)

R and R′ can be either aliphatic or aromatic groups. In this work the diamine chosen was *p*-phenylenediamine: the dianhydride was 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride), and the solvent was *N*,*N*-dimethylformamide (DMF). The poly(amic acid)s were precipitated in a non-solvent, filtered and freeze-dried to remove as much solvent as possible.

The following analytical techniques were utilized in the characterization of samples:

(*a*) Thermogravimetry (TG) of the samples was obtained using a Mettler Vacuum Thermoanalyzer. Analyses were made in platinum crucibles using samples weighing approximately 40 mg. The heating rate was 4°C/min. A dry air flow of about 5.7 liters/h was used.

(*b*) IR spectra of the polymers were obtained using a Beckman IR-12 Infrared Spectrophotometer. The spectra were obtained by preparing KBr pellets of the polymers.

(*c*) Mass spectra were obtained on a Nuclide 12-90 HT Mass Spectrometer. The samples were heated in the instrument by use of a directly heated sample probe. Temperatures were measured by a Chromel–Alumel thermocouple placed in the immediate vicinity of the sample.

DISCUSSION AND RESULTS

Poly (amic acid)s are soluble only in solvents which are capable of very strong polymer–solvent interactions. Consequently, when poly (amic acid)s are precipitated with a non-solvent, solvent molecules remain bound to the polymer molecule. Hatton and Richards[7] found that association of DMF with benzoic acid is probably due to hydrogen bonding between the carbonyl oxygen of the DMF and the hydrogen of the carboxylic acid. The same type of association probably exists in poly (amic acid)s. Kreuz *et al.*[8] have postulated that one mole of their solvent (dimethylacetamide) is associated with each carboxyl function in the poly (amic acid) which they studied.

Since the dissociation energy of hydrogen bonds between the solvent and the polymer is much lower than the dissociation energy of the covalent bonds between atoms in the polymer chain, heating the poly (amic acid) should free the polymer of associated solvent. However, heating a poly (amic acid) causes a ring closure reaction (imidization reaction) to occur (Eqn. 2) with the elimination of water. Thus, a TG curve obtained while heating a poly (amic acid) will show a weight loss due to both the freed solvent molecules and the water eliminated in the polyimide formation.

Fig. 1 shows the behavior of a sample of a poly (amic acid) heated in air. The TG curve shows an initial weight loss which is due to the freed solvent and the water eliminated in imidization. This initial weight loss is followed by a period of constant weight. In this region, all the imide rings which will form should be formed. The polyimide formed from the poly (amic acid) is stable at these temperatures in air. At high temperatures, decomposition begins and continues until the sample is totally decomposed.

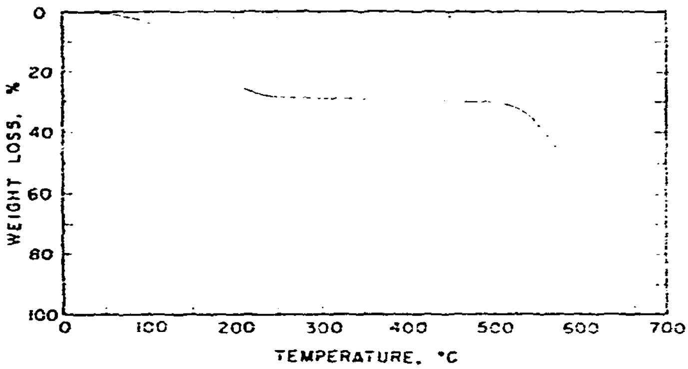
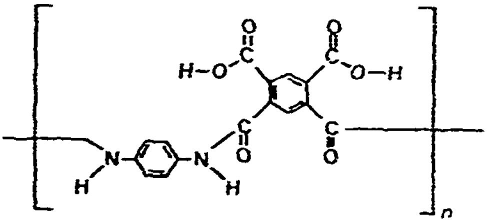


Fig. 1. Thermogravimetry of a poly (amic acid).

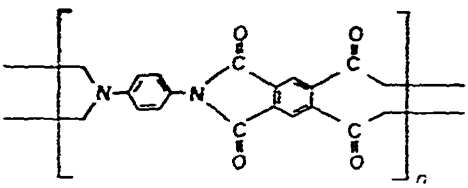
Since the first weight loss region is due only to solvent and water and the second weight loss region is due only to decomposition, the amount of solvent associated in the original poly (amic acid) can be determined through the molecular structures of the poly (amic acid) and polyimide.

The structures of the poly (amic acid) and polyimide expected from the reaction of pyromellitic dianhydride and *p*-phenylenediamine are :



(I)

Poly (amic acid)
Molecular weight
of repeat unit = 326



(II)

Polyimide
Molecular weight
of repeat unit = 290

The molecular weights of the repeat units differ by the molecular weight of the two molecules of water eliminated in the imidization reaction.

When 1.000 g of solvent free poly (amic acid), as represented by structure I, containing *S* g of associated solvent is heated to a temperature sufficient to free all of the solvent and close all of the imide rings but not decompose the polyimide, the weight loss expected is S g of solvent plus 36/326 g of water, or (S+36/326) g.

Defining SW as the original sample weight of poly (amic acid) and WL as the weight loss of the sample due to solvent being freed and water eliminated in the imidization reaction, then the weight loss may be expressed as

$$WL = \frac{SW}{(1+S)}\left(S + \frac{36}{326}\right) \tag{3}$$

Solving for S yields

$$S = \frac{WL - \left(\frac{36}{326}\right)SW}{(SW - WL)} \times \frac{\text{mass of solvent}}{\text{mass of poly(amic acid)}} \tag{4}$$

In order to be more precise in all TG solvent determinations, the temperature was raised linearly at 4°C/min to 350°C. The sample was held at 350°C to insure that all solvent had been freed and that all rings that would close had closed. A linear heating rate of 4°C/min was again utilized from 350°C to total decomposition. Weight losses needed in Eqn. 4 were obtained from the TG curves. Fig. 2 shows the TG curve used for obtaining the data required in Eqn. 4. For simplicity only the general TG curve is shown: however, all calculations were based upon the expanded TG.

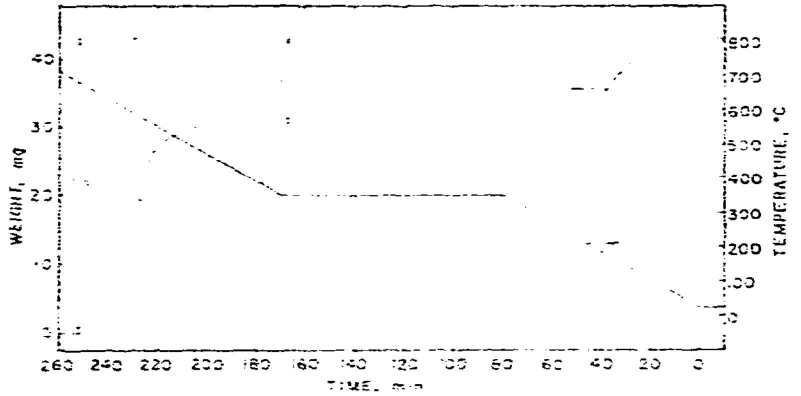


Fig. 2. TG curve used in conjunction with Eqn. 4.

The poly (amic acid)s analyzed by the above method have been found to contain between 0.2 and 0.3 g DMF/g poly (amic acid). Reproducibility on a given sample has been found to be ±0.005 g DMF/g poly (amic acid).

When a sample of poly (amic acid) was exposed to high vacuum, some of the solvent was freed from the polymer molecule. In order to check the validity of the method, a sample of poly (amic acid) containing associated solvent was exposed to

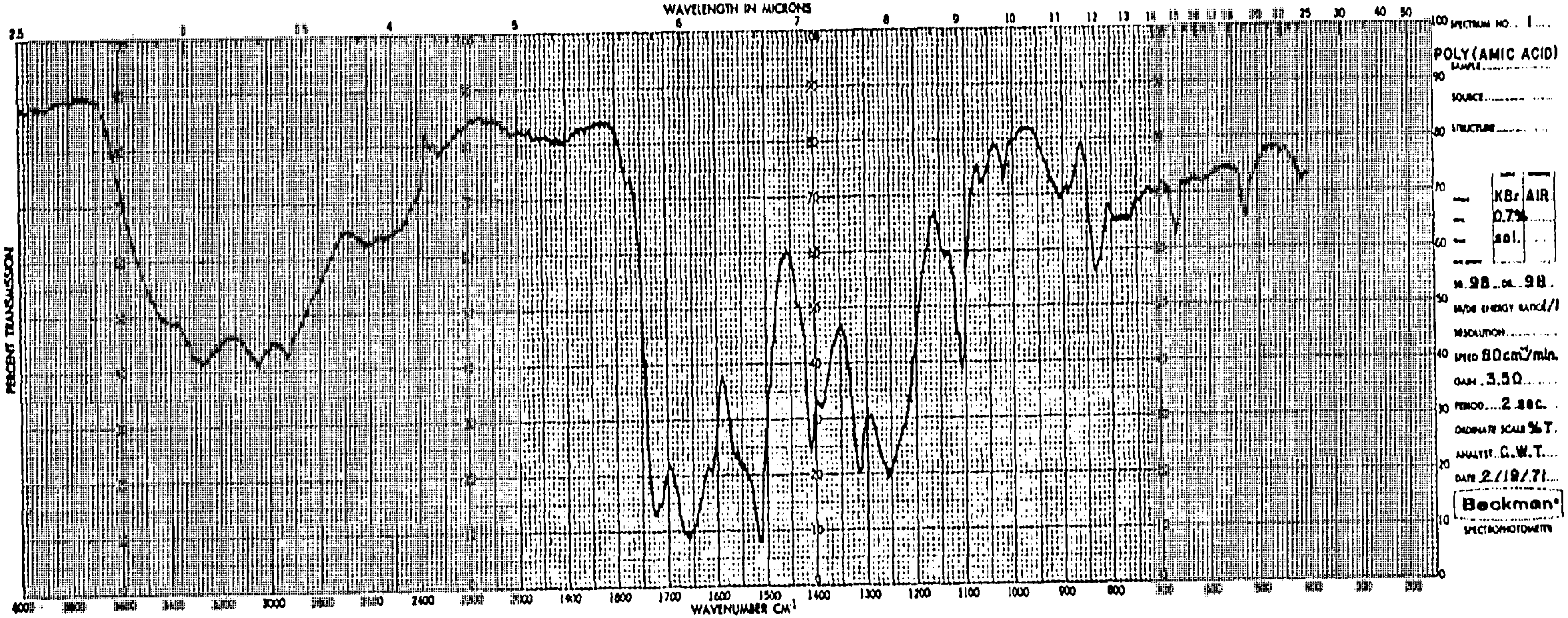


Fig. 3. Infrared spectrum of poly (amic acid).

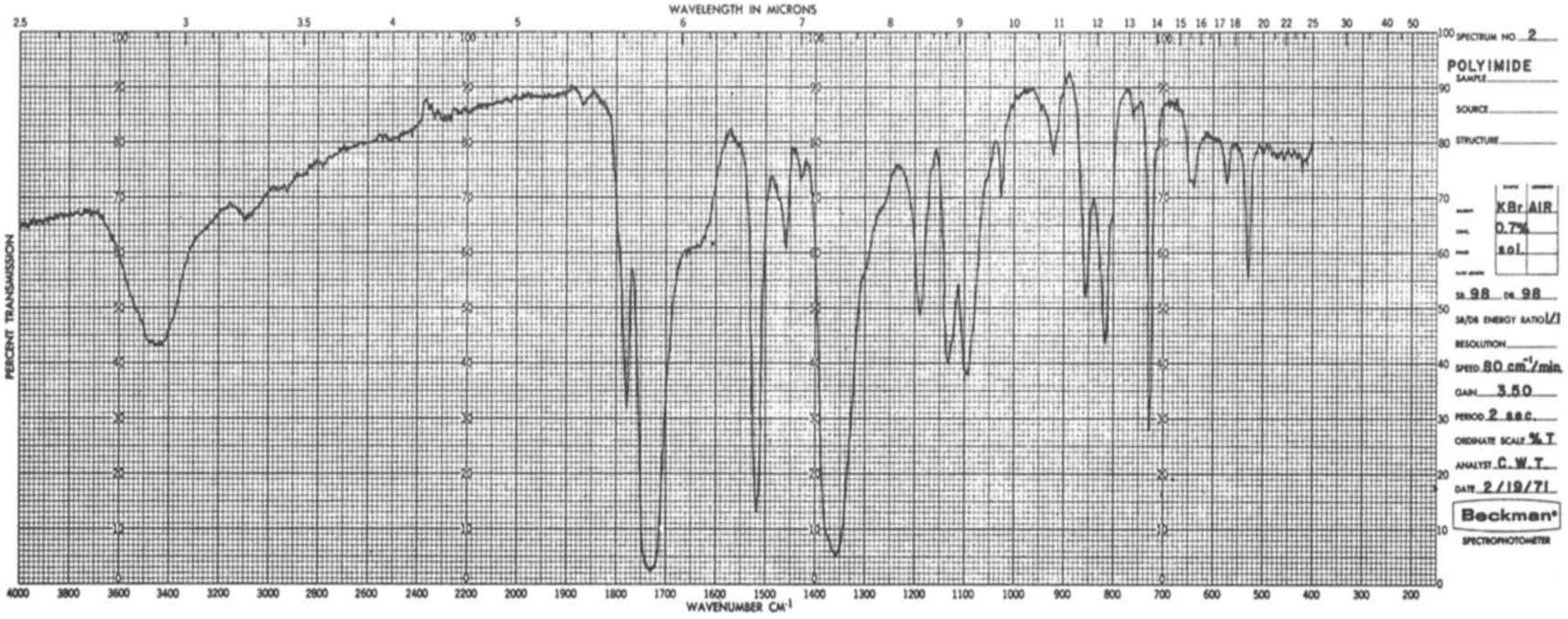


Fig. 4. Infrared spectrum of polyimide.

vacuum overnight, the pressure ranging from 10^{-6} to 10^{-7} torr. The sample lost 15.2% of its weight. The amount of associated solvent was determined by TG before and after vacuum treatment. The sample contained 0.2786 g solvent/g poly (amic acid) before vacuum treatment and 0.0861 g solvent/g poly (amic acid) after being exposed to vacuum. The percentage weight loss of solvent from the original sample by the TG measurements was 15.1%, which is in excellent agreement with the experimentally measured weight loss.

The method makes no allowance for end groups where only one water molecule is lost per repeat unit. End group effects will become negligible as the chain length increases; therefore, the method will improve in accuracy with higher molecular weight polymers.

We have assumed that the structures of the poly (amic acid) and polyimide are represented by the structures I and II. Figs. 3 and 4 are IR spectra of the poly(amic acid) and polyimide, respectively. The IR spectrum of the poly (amic acid) contains absorption bands at 3280–3320 cm^{-1} (NH stretch), 1660 cm^{-1} (amide I), 1550 cm^{-1} (amide II), 1725 cm^{-1} (carboxyl C–O stretch), 1410 and 905 cm^{-1} (OH deformations) and 1315 cm^{-1} (C–O stretch) confirming the structure of the poly(amic acid). A minor peak at 1779 cm^{-1} indicates the presence of small amounts of imide linkages. In the IR spectrum of the polyimide, the bands characteristic of carboxylic acid and secondary amide have disappeared and bands characteristic of imide at 1779, 1730 and 725 cm^{-1} have appeared.

Complete ring closure to polyimide has been assumed in developing our equation. Because of steric conditions, some uncyclized units may be present in the polyimide. Estimates have been made that there is one uncyclized ring per eight or nine polymer repeat units[9]. This can result in a maximum error of less than 2% in the calculation of associated solvent if it is assumed that one uncyclized ring is present per eight polymer repeat units and that two moles of DMF are associated with one poly (amic acid) repeat unit. A shoulder in the IR spectrum of the polyimide at 1650 cm^{-1} and elemental analysis of the polyimide indicate that there may be some uncyclized rings remaining in the polyimide. The following elemental analysis of the polyimide* is included for comparison with the calculated structure. Calc.: C, 66.21%; H, 2.08%; N, 9.65%. Found: C, 64.63%; H, 2.22%; N, 9.59% (Anal. 1); C, 64.65%; H, 2.13% (Anal. 2).

In order to determine the products evolved on heating the poly (amic acid), a sample was heated in a sample probe in a mass spectrometer. Samples of DMF showed the three most intense peaks to be mass numbers 29, 44 and 73. Mass number 18 was the most intense peak for water. Fig. 5 shows the decrease in DMF and water evolved from a sample of poly (amic acid) as a function of temperature. There were no indications of polymer decomposition during the heating process. These results along with the TGA trace confirm that below 350°C DMF and water are the only gaseous products evolved from the heating of the poly (amic acid).

---

*Spang Microanalytical Laboratory, Ann Arbor, Michigan 48106.

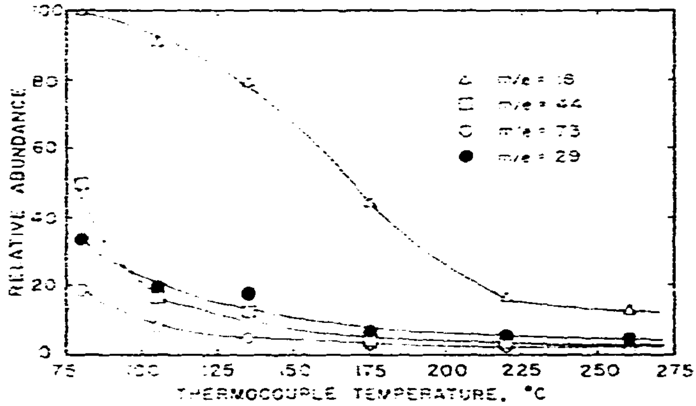


Fig. 5. Mass spectral data obtained from heating a poly (amic acid) sample.

CONCLUSIONS

The foregoing method is valid for the determination of the amount of associated solvent in poly(amic acid)s which are formed from diamines and dianhydrides, and with other types of polymers which have solvents associated with the polymer chains. The method requires a final polymer of sufficient thermal stability so that solvent removal and any cyclization reactions (or curing reactions) occur before the onset of decomposition.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Gordon Lewis and Mrs. Margaret Biolsi (GCMR, University of Missouri–Rolla, Rolla, Mo.) for their assistance in obtaining the mass spectra. The financial support of this work by Western Electric Company is acknowledged.

REFERENCES

1 G. M. Bower and L. W. Frost, *J. Polymer Sci. A*, 1 (1963) 3135.
2 C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards and K. L. Oliver, *J. Polymer Sci. A*, 3 (1965) 1373.
3 R. A. Dine-Hart and W. W. Wright, *J. Appl. Polymer Sci.*, 11 (1967) 609.
4 C. E. Sroog, *J. Polymer Sci. C*, 16 (1967) 1191.
5 W. M. Edwards, U. S. Pats. 3,179,614 and 3,179,634 (April 20, 1965).
6 A. L. Endrey, U. S. Pats. 3,179,631 and 3,179,633 (April 20, 1965).
7 J. V. Hatton and R. E. Richards, *Mol. Phys.*, 3 (1960) 253.
8 J. A. Kreuz, A. L. Endrey, F. P. Gay and C. E. Sroog, *J. Polymer Sci. A-1*, 4 (1966) 2607.
9 D. P. Bishop and D. A. Smith, *J. Appl. Polymer Sci.*, 14 (1970) 345.