Thermochimica Acta, 134 (1988) 145–153
Elsevier Science Publishers B.V., Amsterdam

POLYAMIC ACID ESTERS CHARACTERIZED BY THERMOGRAVIMETRIC ANALYSIS

Bonnie J. Bachman and Frank M. Houlihan

AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974-2070 (USA)

ABSTRACT

Novel alkyl esters of oxydianiline/pyromellitic dianhydride polyamic acid have been synthesized using a coupling agent reaction. These alkyl esters were prepared as the pure meta and para polymers. The cure behavior of these polymers was studied using thermogravimetric analysis and compared to that of both the parent polyamic acid and its methyl ester. Curing was found to be similar to that of the parent ODA-PMDA, but the data shows that the isomeric esters have a lower onset of reaction temperature as well as a narrower reaction range than the methyl ester. It was also shown than differences between theoretical and experimental weight loss are significantly larger for ODA-PMDA polyamic acid than for either the isomeric esters or the methyl ester.

INTRODUCTION

Previous work on polyamic acid esters has focused on polymers derived from linear alkyl alcohols using acid chloride in an intermediate synthesis step.[1-8] These polyamic acid alkyl esters were observed to have increased room temperature solution stability as a result of the protection of the carboxylic acid group by the ester.[4-7] Although an increase in solution stability was achieved, polyamic acid alkyl esters synthesized to date have been found to cure more slowly than the corresponding free polyamic acids.[4] In addition to a reduced cure rate, the release of alcohol at high temperatures can have detrimental effects on the molecular weight

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

and thereby influence the physical properties of the resulting polyimide. Work was begun to synthesize a polyamic acid ester that contains a protecting group which can be readily removed during cure, thus making the cyclization of the acid the rate-determining step rather than the cyclization of the ester. Characterization by thermogravimetric analysis (TG) will be discussed for novel isomeric polyamic acid esters and methyl esters.

EXPERIMENTAL

Alkyl esters based on polyamic acid from pyromellitic dianhydride (PMDA) and oxydianiline (ODA) were synthesized using coupling agent chemistry described by Houlihan and co-workers.[9] As a result of this coupling agent process, pure isomers of alkyl esters were able to be isolated. Solvents and water were removed from the samples by placing them in a drying pistol with a quantity of phosphorus pentoxide. The assembly was under vacuum and held at a constant temperature of 68°C while refluxing methanol for 16 hours. Three types of alkyl esters were characterized, including polyamic acid derived from methyl esters in addition to the novel meta-R and para-R esters. These R-esters have not been reported in the literature and represent a new class of polyamic acid esters. N-methylpyrrolidone was used as a solvent in the preparation of the polymers.

Thermogravimetry (TG) studies were performed on a Perkin-Elmer TGS-2 thermogravimetric analyzer interfaced with a System 4 microprocessor for temperature programming and a TADS Model 3700 data station for data acquisition and operational control. All measurements were obtained in N_2 with a gas flow rate of 30 cc per minute. Heating rates used for the dynamic study were 5 and 25 °C per minute. All samples were pulverized and masses ranged between 2.70 and 3.10 mg. Representative TG and derivative TG (DTG) curves are shown in Figure 1. Additionally, assignments for onset temperature, T_i, and maximum rate of reaction, T_{MAX}, are included.

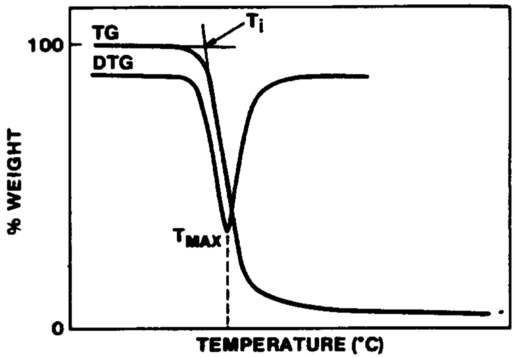


Figure 1

EXPERIMENTAL METHOD
THERMOGRAVIMETRIC ANALYSIS (TG)

RESULTS AND DISCUSSION

Figure 2 depicts schematically the classical method for synthesizing esters of polyamic acid. An alternate pathway for the synthesis of alkyl esters using coupling agent chemistry was devised and applied successfully. Polyamic acid esters will be discussed which have been prepared by this alternative route. Meta and para isomers were isolated by recrystallization at an intermediate stage in the synthesis and verified by ^{1}H and ^{13}C NMR.[9]

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves using a heating rate of 25°C per minute for ODA-PMDA polyamic acid and its esterified meta-R ana para-R isomeric products are shown in Figure 3. It can be seen that the ODA-PMDA polyamic acid TG curve (Figure 3.a) has a broader region for weight loss and a slightly higher minimum (maximum rate of reaction) in the DTG curve than the esterified products. Figure 3 also shows the asymmetric shaped DTG curves for the isomeric esters (Figures 3.b and 3.c) compared with the symmetric derivative obtained for polyamic acid. Additionally, the maximum rate of reaction can been seen to occur earlier for the isomeric esters than for the polyamic acid. The asymmetric shaped DTG curves for the R ester may be explained by multiple reaction steps

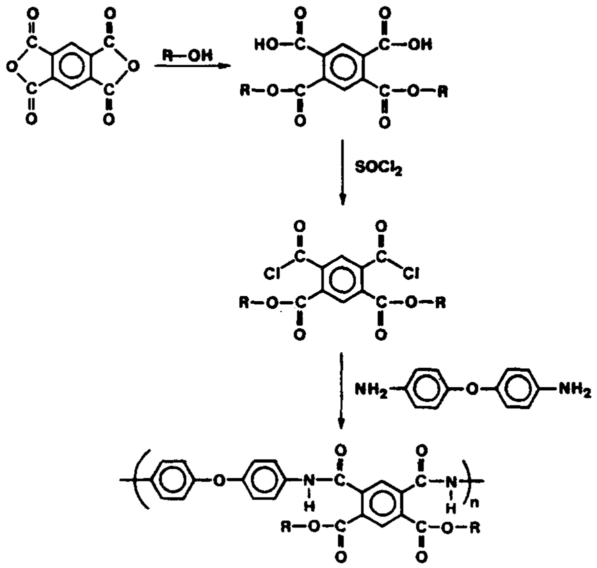
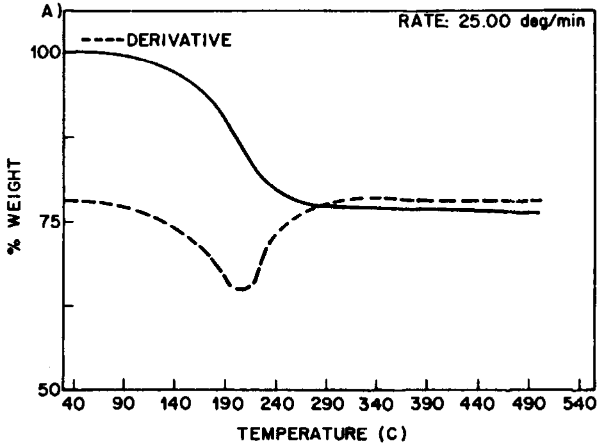


Figure 2
CLASSICAL METHOD FOR PRODUCING ESTERS OF POLYAMIC ACID

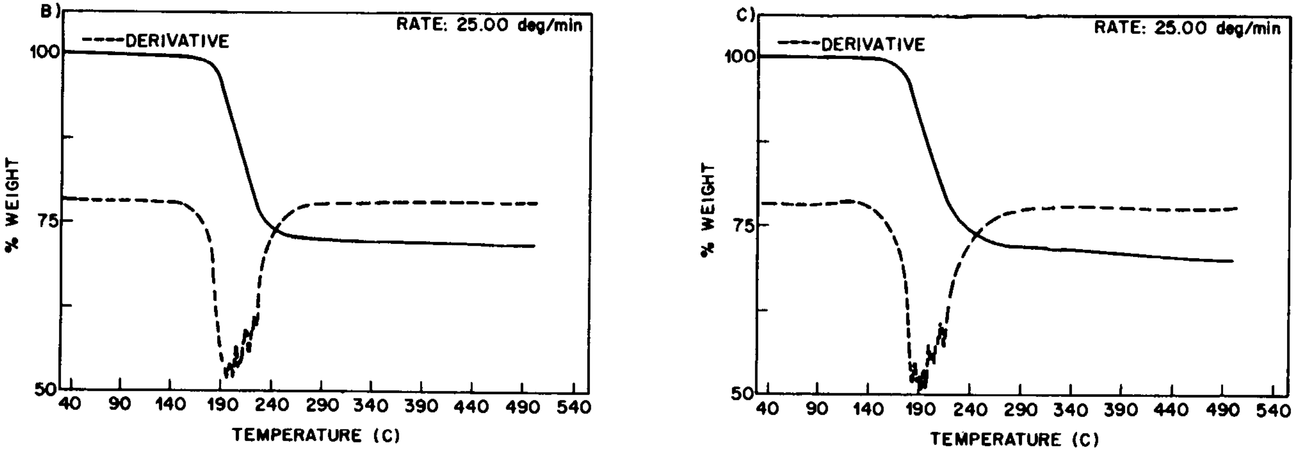
that may include an initial rapid deprotection of the R group. The three TG curves shown in both Figures 4 and 5 illustrates the broad reaction range of the ODA-PMDA polyamic acid in comparison to the isomeric R esters. Samples which were heated at a rate of 25 °C per minute and had not undergone solvent removal procedures are shown in Figure 4. Using a heating rate of 5 °C per minute and removing solvent prior to running the dynamic TG are displayed in Figure 5.

Table 1 summarizes the maximum rate of reaction, onset temperature, and weight loss percent at 495°C for the ODA-PMDA polyamic acid as well as the para-R and meta-R isomers. Additionally, a comparison of before and after solvent removal data is provided.

Theoretical weight loss for the elimination of water, shown in Table 1, for ODA-PMDA polyamic acid is 8.61%. This is contrasted with the actual weight loss obtained before and after solvent removal of 23.9% and 13.1%, respectively. Although there are heating rate differences, the ODA-PMDA polyamic acid still exhibits a larger weight loss value before and



ODA-PMDA



p-R ESTER

m-R ESTER

Figure 3

TG AND DTG CURVES FOR POLYAMIC ACID AND POLYAMIC ACID ESTERS

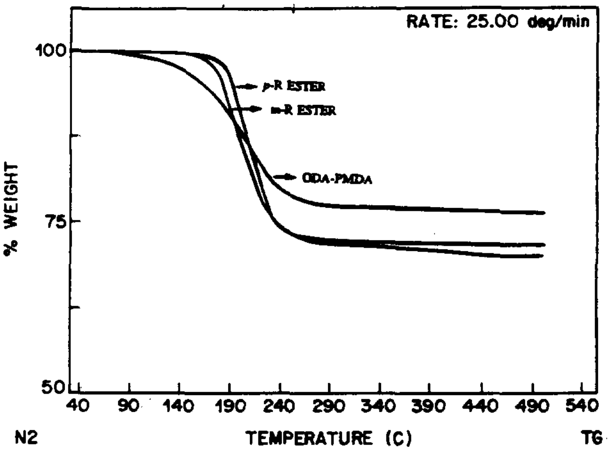


Figure 4

TG CURVES FOR POLYAMIC ACID AND POLYAMIC ACID ESTERS

Table 1

TG Analyses of ODA-PMDA Polyamic Acid and Its Esterified Products

Polymer	Heating Rate (°C per min)	Condition	Onset Temperature (°C)	Maximum Rate of Reaction (°C)	Weight Loss (Theory) %	Weight Loss (Actual) %
ODA-PMDA	25	Solvent	153	202	8.61	23.9
p Ester	25	Solvent	183	197	27.9	28.3
m Ester	25	Solvent	173	190	27.9	30.0
Methyl Ester	25	Solvent Removed	192	212	15.3	14.8
ODA-PMDA	-			-	-	-
p Ester	5	Solvent	164	178	27.9	28.6
m Ester	5	Solvent	155	167	27.9	30.0
ODA-PMDA	5	Solvent Removed	150	186	8.61	13.1
p Ester	5	Solvent Removed	163	178	27.9	27.2
m Ester	5	Solvent Removed	153	169	27.9	29.9

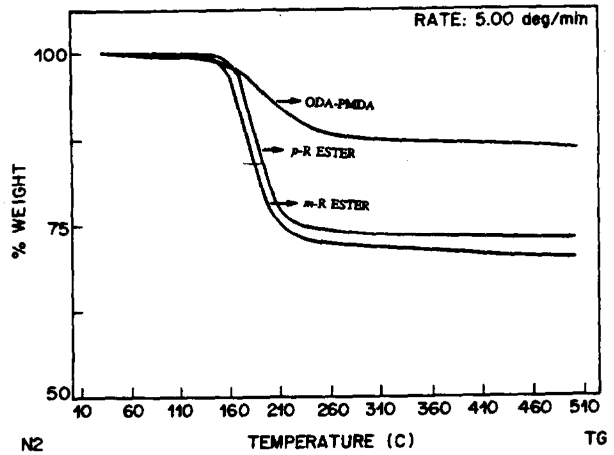


Figure 5
TG CURVES FOR POLYAMIC ACID AND POLYAMIC ACID ESTERS

after solvent removal when compared to the theoretical value. Solvation of the polyamic acid by NMP could account for these larger weight losses as well as the presence of oligomers formed during the subsequent precipitation and drying procedures. Conversely, both isomeric polyamic acid esters approach their theoretical weight loss of 27.9% irrespective of solvent removal processes. Figure 5 compares the three TG curves obtained at a heating rate of 5°C per minute after undergoing solvent removal and drying.

The para-methyl diester of ODA-PMDA had a weight loss of 14.8% at 495°C compared to the theoretical value of 15.3%. Onset of weight loss for this polymer, at a heating rate of 25°C per minute, was 191.6°C with a maximum rate of reaction of 211.5°C. As was the case for the polyamic acid samples, the DTG curve for this polymer is symmetric. The methyl ester has a higher onset and maximum rate of reaction when compared to ODA-PMDA polyamic acid and the para-R and meta-R esters, indicating that the R ester falls intermediate between ODA-PMDA polyamic acid and its methyl ester in ease of imidization.

CONCLUSIONS

Polyamic acid alkyl esters of ODA-PMDA have been synthesized using coupling agent chemistry as opposed to the classical route which incorporates acid chlorides. Isomeric alkyl esters prepared by this novel synthetic route can be isolated and TG studies on these isomeric products have been performed. TG data shows that the novel R-esters have a lower T_i and a narrower reaction range than the methyl ester. This data has implications for the cyclization of polyamic acids, since alkyl esters have previously been reported to cure substantially more slowly than the corresponding free acids. Differences in DTG between the two alkyl esters indicate multiple reactions occur for the R-esters (i.e. deprotection of the R-group followed by cyclization of the resulting polyamic acid), while methyl esters only exhibit a single reaction mechanism, that of cyclization of the acid ester. Differences between theoretical and experimental weight loss are significantly larger for ODA-PMDA polyamic acids than for the alkyl esters. It has been proposed that solvation of the polyamic acid by NMP could account for those larger weight losses as well as the presence of oligomers.

REFERENCES

1. S. N. Kharkov, S. V. Vinogradova, Ya. S. Vygodskii and Z. V. Gerashchenko, Vysokomol Soyed, 13, 1190 (1971).
2. S. N. Kharkov, Ye. P. Krasnov, Z. N. Lavrova, S. A. Baranova, V. P. Aksevova and A. S. Chegolya, Vysokomol Soyed, 13, 833 (1971).
3. Ye. D. Molodtsova, G. I. Timofeyeva, S. S. A. Pavlova, Y. S. Vygodskii, S. V. Vinogradova and V. V. Korshak, Vysokomol Soyed, 19, 346 (1977).

4. S. Nishizaki and T. Moriwaki, Kogyo Kagaku Zasshi, **73** (8), 1873 (1970).

5. S. Nishizaki and T. Moriwaki, Industrial Chemistry Magazine,**71**, 1559 (1968).

6. V. V. Kudryavtsev, M. M. Koton, T. K. Meleshko and V. P. Sklizkova, Vysokomol Soyed, **A17** (8) 1764 (1975).

7. A. I. Koltsov, S. A. Dauengauer, V. M. Denisov, L. A. Shibaev, Yu. N. Sazanov, M. K. Bukina and M. M. Koton, Doklady Akademii Nauk SSSR, **278** (6), 1380 (1984).

8. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev and L. A. Laius, *Polyimides-Thermally Stable Polymers*, (Plenum Press, New York, 1987.

9. F. M. Houlihan, B. J. Bachman, C. A. Pryde and C. W. Wilkins, Jr., Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, to be published.