

Preparation of oligo-arylamides and their characterization by reaction calorimetry

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Abstract

The synthesis of oligomeric arylamides was carried out in a reaction calorimeter by low temperature interfacial polycondensation. The on line measurements of the evolved heat under different reaction conditions allowed us to estimate both kinetic and thermodynamic parameters. A complex mechanism seems to take place, involving the formation of co-monomeric species, their coupling and/or the monomeric attach on the initially formed condensation product.

A proper choice of both the synthetic procedure and the related experimental parameters (temperature, concentration of reagents and their initial molar ratio, stirring rate, etc.), allows to induce structural modifications in the resulting oligomeric species. The process was optimized in terms of yields, distribution of end groups and average molecular masses, as a function of thermochemical data.

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Keywords: Oligomeric arylamides; Reaction calorimetry; Thermodynamic data; Molecular masses; End groups

1. Introduction

The widespread interest to develop environmentally benign processes lead to investigate the usefulness of selected organic macromolecules, such as polystyrene, as supports to reagents and catalysts in some chemical processes. It has already been demonstrated that many transition elements (Pd, Pt, Rh, etc.) immobilized on polymers offer a number of advantages over traditional solution phase catalyzed chemical reactions [1,2].

In this context, oligomeric organic species of different molecular structure may represent a valid alternative to the ever increasing applications in the field of the so-called “heterogenized organometallic catalysis” [3–5].

Our previous studies were concerned with the syntheses of oligomeric aromatic amides whose structure and functionalities would make them suitable to be active part in a catalytic system of high performance when applied to or-

ganic processes of industrial interest, such as hydrogenation, oxidation, etc. [6–8]. One of the most representative terms of this class, namely the oligo-1,4-phenylene-terephthalamide (OPTA), is structurally similar to Kevlar, although its lower average molecular mass (\overline{MM} in the range 800–2500 amu) implies a significant relative amount of the end groups ($-NH_2$ and $-COOH$), capable to link coordinatively with most catalytically active elements [9].

A complete characterization of OPTA is however a rather difficult task, in that it proved to be insoluble in all common solvents and is also highly stable towards chemical, thermal and mechanical stresses [10,11]. This paper reports our investigations on the synthesis of the title oligomers by emulsion polycondensation; a reaction calorimeter was used which records the evolved heat and accounts for the related thermodynamic and kinetic data [12,13]. This will allow to establish the relationships between the optimized preparative procedure leading to OPTA, its structure and the related physical and chemical properties. On the other hand, a proper choice of the experimental conditions will make it possible to modify the structural characteristics of the oligomeric species, in terms of \overline{MM} and distribution of functional groups.

Abbreviations: OPTA, oligo-1,4-phenyleneterephthalamide; PDA, 1,4-phenylenediamine; TPC, terephthaloyl chloride; amu, atomic mass units; visc, viscosimetric; titr, titrimetric; rpm, runs per minute

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Nomenclature

| | |
|-----------------|---|
| AR | addition rate (l min^{-1} or mol min^{-1}) |
| C | conversion (ratio between the Q_r at time t and the Q_r at the end of the reaction) (%) |
| ΔH | reaction enthalpy (kJ mol^{-1}) |
| \overline{MM} | average molecular mass (amu) |
| Q | evolved heat at the end of reaction (kJ g^{-1}) |
| Q_r | evolved heat during the reaction (kJ) |
| SR | stirring rate (rpm) |
| T_j | temperature of heating jacket (K) |
| T_R | reaction temperature (K) |

2. Experimental

2.1. Preparation of OPTA and calorimetric measurements

The synthesis of OPTA ($T_g = 515\text{--}570\text{ K}$) and other similar oligomeric arylamides, was carried out by low temperature emulsion polycondensation, in a reaction calorimeter Mettler Mod. RC1, equipped with a 21 glass reactor mod. AP01; a terephthaloyl chloride solution in cyclohexanone (TPC, 0.108 mol l^{-1}) was added to an aqueous solution of 1,4-phenylenediamine (PDA, 0.150 mol l^{-1}), according to a previously reported procedure [9]. The overall heat evolved (Q_r), was calculated taking into account all related contributions, such as the experimental value, the sensible heat accumulated and the additional value resulting from mixing and stirring of the reagents, together with the subtractive factor due to the instrumental losses. The process variables, i.e., inner temperature of the reactor (T_R), temperature of the heating jacket (T_j), stirring rate (SR), etc., were monitored and acquired on line through an IBM PS2/80 computer, in QNX language. A precision balance Mettler mod. PM 1200 and a piston pump Prominent mod. Gamma/4W are linked to the computer by an interface RD10, to maintain the established addition rate of reagents [13].

2.2. Gravimetric yield

It has been defined as the amount of OPTA (by weight), resulting after each test run.

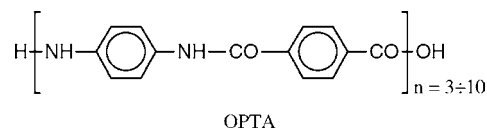
2.3. Average molecular mass determination

The average molecular mass (\overline{MM}) of OPTA was determined both by viscosimetric ($\overline{MM}_{\text{visc}}$) and titrimetric ($\overline{MM}_{\text{titr}}$) methods, as already reported [6]. The $\overline{MM}_{\text{visc}}$ data were obtained in a Desreux-Bischoff viscosimeter, by measuring the time of flow of a given volume of a sulphuric acid solutions of the oligomer. The other method is based on either acid (HCl) and basic (NaOH) titrations; the results were reported as a number of stoichiometrically basic and acid groups per mole of dried OPTA. Both methods give

comparable \overline{MM} values, ranging from 800 to 2500 amu obtained as the arithmetic mean of several measurements. The set of experimental conditions adopted in the calorimetric reactor gives an oligomeric species whose \overline{MM} is near the lowest range (~ 800 amu).

3. Results and discussion

The calorimetric data obtained during the preparation of OPTA indicate the amount of evolved heat (Q) and its time dependence (Q_r); these data, together with yields, average molecular masses and distribution of acid and basic end groups of the oligomeric species, have been correlated to the main reaction parameters, such as temperature, stirring and addition rates, concentration of reagents and their initial molar ratio. Figs. 1–7 show the results of all experimental tests carried out in the calorimetric reactor



3.1. Reaction temperature (T_R)

The reaction investigated was carried out at different temperatures in the range $273\text{ K} \leq T_R \leq 303\text{ K}$. As shown in

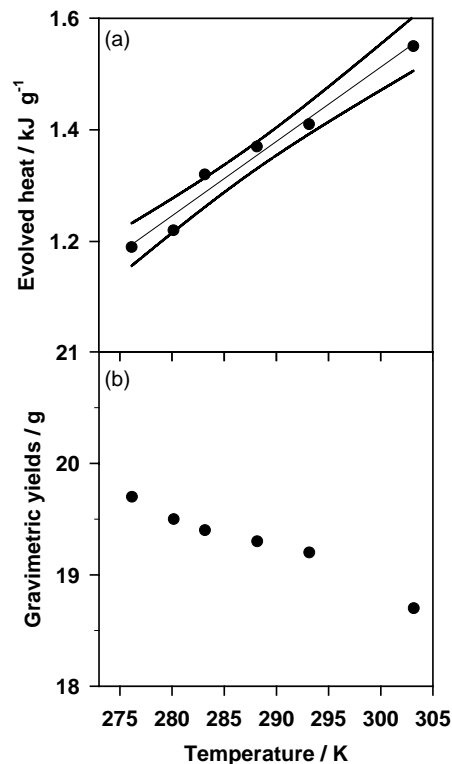


Fig. 1. Temperature effect on (a) evolved heat and (b) gravimetric yields of OPTA. Experimental conditions: $[\text{PDA}]/[\text{TPC}] = 1.4\text{ mol mol}^{-1}$; $\text{SR} = 300\text{ rpm}$; $\text{AR} = 0.75\text{ l}_{\text{TPC}}\text{ h}^{-1}$; $[\text{PDA}]_{\text{initial}} = 0.15\text{ M}$.

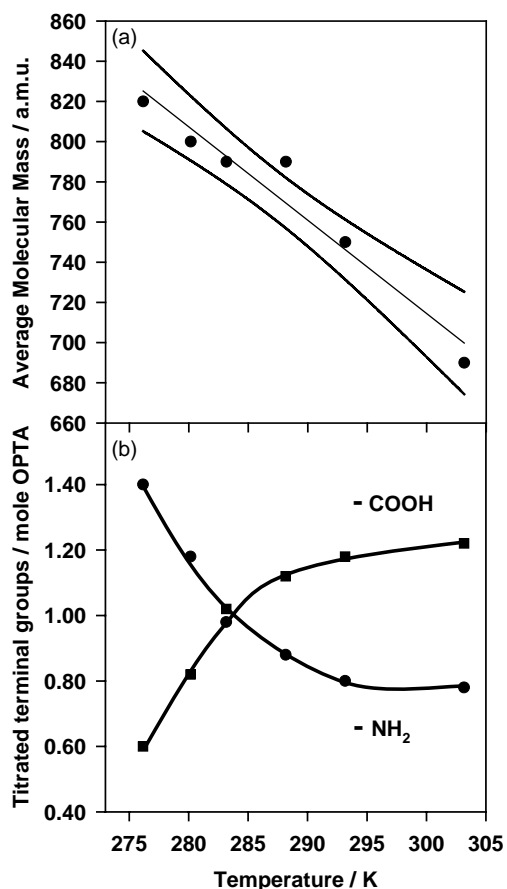


Fig. 2. Temperature effect on (a) $\overline{MM}_{\text{visc}}$ and (b) distribution of end groups in the OPTA. Experimental conditions: $[\text{PDA}]/[\text{TPC}] = 1.4 \text{ mol mol}^{-1}$; $\text{SR} = 300 \text{ rpm}$; $\text{AR} = 0.75 \text{ l}_{\text{TPC}} \text{ h}^{-1}$; $[\text{PDA}]_{\text{initial}} = 0.15 \text{ M}$.

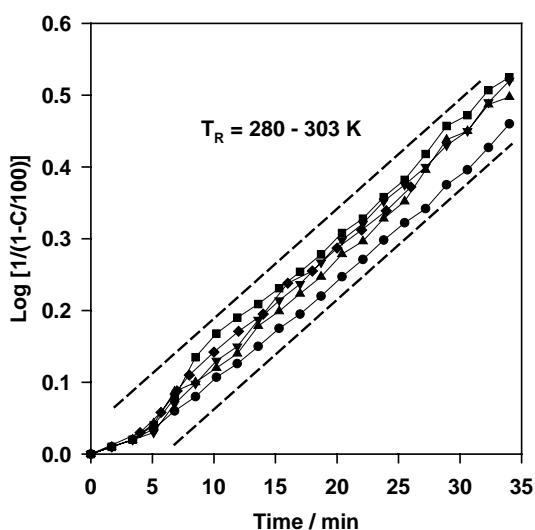


Fig. 3. Reaction conversion (as derived from the evolved heat) vs. time. Conversion is assumed to be complete when heat production stops. $T_r = 280 \text{ K}$ (▲), $T_r = 283 \text{ K}$ (■), $T_r = 288 \text{ K}$ (◆), $T_r = 293 \text{ K}$ (●), $T_r = 303 \text{ K}$ (▼).

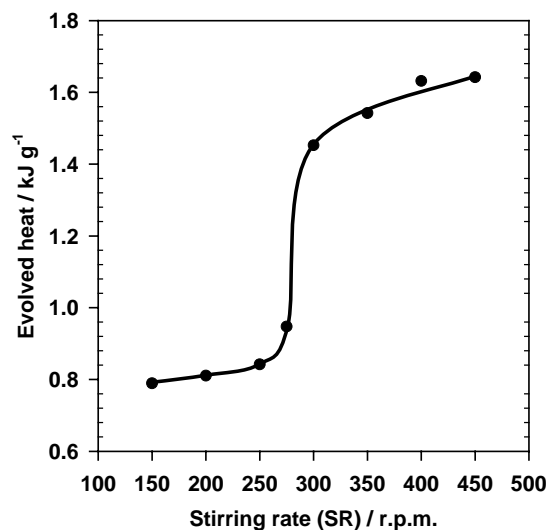


Fig. 4. Evolved heat as a function of the stirring rate SR. Experimental conditions: $T_r = 283.16 \text{ K}$; $[\text{PDA}]/[\text{TPC}] = 1.4 \text{ mol mol}^{-1}$; $\text{AR} = 0.75 \text{ l}_{\text{TPC}} \text{ h}^{-1}$; $[\text{PDA}]_{\text{initial}} = 0.15 \text{ M}$; up-flow stirring device used.

Fig. 1a, the heat produced for each weight unit of OPTA increases linearly with the temperature, whereas the yields of reaction are negatively affected by the rise of T_R (Fig. 1b). Furthermore, the temperature of reaction influences either the degree of oligomerization as well as the distribution of end groups, as shown in Fig. 2. In detail, relatively higher T_R give low \overline{MM} oligomeric species (Fig. 2a) where -COOH groups predominate (Fig. 2b), while at lower T_R oligomers with high \overline{MM} and a prevailing distribution of -NH₂ groups are obtained. In other words, an increase of T_R corresponds to oligomers of lower \overline{MM} and low gravimetric yields (Fig. 1b), although a larger number of bonds is formed; accordingly, a greater amount of heat is produced.

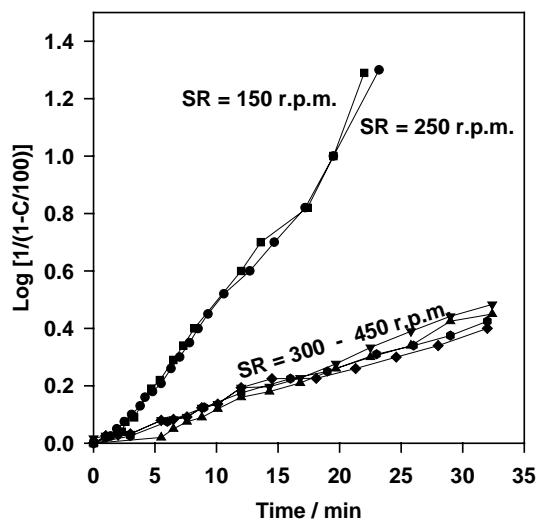


Fig. 5. Conversion to OPTA as a function of the stirring rate SR. Reaction rate conditioned by TPC diffusion below $\text{SR} = 250 \text{ rpm}$. Experimental conditions: see Figs. 3 and 4.

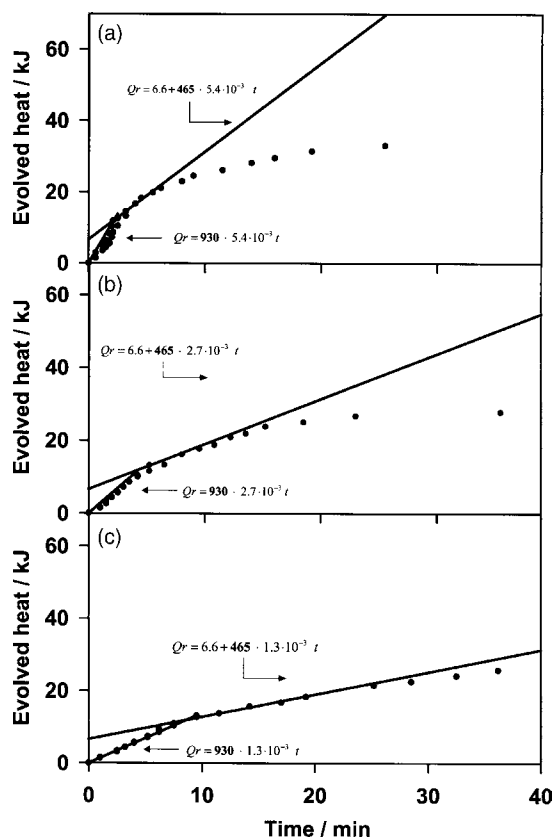


Fig. 6. Evolved heat as a function of time, at different addition rates. Direct relationship between the slope and the addition rate AR: (a) $AR = 5.4 \times 10^{-3} \text{ mol}_{\text{TPC}} \text{ min}^{-1}$; (b) $AR = 2.7 \times 10^{-3} \text{ mol}_{\text{TPC}} \text{ min}^{-1}$; (c) $AR = 1.3 \times 10^{-3} \text{ mol}_{\text{TPC}} \text{ min}^{-1}$.

These effects have been rationalized in terms of a different kinetic influence of the reaction temperature on the rate of the two concomitant processes which occur in the reaction medium, i.e., formation of amide bonds versus hydrolysis of terephthaloyl chloride, the rate of the former reaction being presumably less influenced by the T_R .

As far as the reaction kinetics are concerned, it is worth noting that the rate of heat production does not appreciably depend on the temperature, at least in the limited T_R range investigated. In fact, assuming the rate depends on the first power of the concentration, there are no significant changes in the slopes of the straight lines associated with the almost linear kinetic function $(1/\log(1 - C/100)) = f(t)$ (Fig. 3).

3.2. Stirring rate (SR)

Noteworthy, both the evolved heat and its production as a function of time are strongly dependent on the stirring rate SR (Figs. 4 and 5). The latter factor also affects the yield of the oligomerization reaction. In Fig. 5 it is evident that the conversion to OPTA grows proportionally as the SR increases. In both cases there is a sharp discontinuity condition around a value of SR ~ 275 rpm; below this value the reaction slows down and the heat evolved decreases alike.

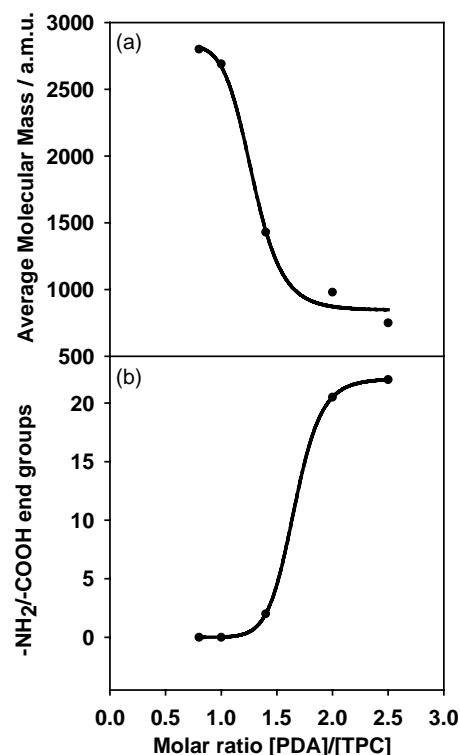


Fig. 7. Influence of [PDA]/[TPC] on (a) \overline{MM} and (b) $-NH_2/-COOH$ distribution.

The apparently anomalous slopes of functions in Fig. 5 (i.e., conversion values inversely proportional to the stirring rates) can be evaluated by considering that the calorimetric conversion ($\Delta H_t/\Delta H_{\text{end}}$) differs from the real conversion because the latter does not correspond to the instrumental “end point”.

From an experimental point of view, a double layer is observed inside the calorimetric reactor, at low stirring rates. This phase separation between the two immiscible solutions containing each the reagents involved in the reaction, corresponds to a minimum of the contact area. Therefore, transfer rate becomes a conditioning factor for the kinetics of the whole oligomerization process and the mutual dispersion of each phase is strongly influenced by the stirring rate.

3.3. Addition rate of reagents (AR)

The patterns of evolved heat as a function of time, at three different addition rates of the TPC organic solution to the aqueous PDA (Fig. 6a and c), were interpolated by a graphic function to obtain a series of straight lines where the slope of the tangent to the experimental curves is for each point directly proportional to the evolved heat power. This function represents a consecutive kinetic process within a stepwise reaction pathway.

The equations of the straight lines related to the experimental patterns of Fig. 6, were calculated assuming that:

- (a) During the first stage two amide bonds are formed when each TPC molecule reacts with PDA; this reaction step yields a condensation product with three aromatic rings and two amino end groups, whose heat of formation is close to $930 \pm 20 \text{ kJ mol}^{-1}$ of TPC. Thereafter, a mass balance indicates that almost 30 mmol of PDA have been already used in the condensation product, whereas almost 85 mmol of it remain unreacted in the aqueous solution, as derived from the intercept to the Q_r axis.
- (b) Other reaction steps follow, involving the formation of one bond for every TPC molecule added ($\Delta H \sim 465 \text{ kJ mol}^{-1}$).
- (c) The slope of each plot $Q_r = f(t)$ (Fig. 6) is then given by the product of two terms, i.e., the amount of heat per mole of TPC ($\Delta H \sim 930$ or 465 kJ mol^{-1}) and the addition rates ($AR = 5.4 \times 10^{-3}$, 2.7×10^{-3} and $1.3 \times 10^{-3} \text{ mol min}^{-1}$). Obviously, the AR values result from the product of the concentration of the TPC solution added (0.108 M), its flow rate ($AR = 0.75$, 1.50 or 3.00 l h^{-1}) and the appropriate conversion factor 1/60.

The proposed polycondensation sequence should then involve the initial fast formation of a three rings co-monomeric species, i.e., where two amide bonds are formed for each mole of added TPC, followed by their mutual coupling and/or the attack of monomers (PDA and TPC) on the chain condensation product already formed. The pattern of experimental curves in Fig. 6 indicates that in all cases a sharp slowing down occurs in the rate of these chain lengthening steps leading to the oligomeric species. It is worth noting that, despite an excess of free PDA, the chain lengthening reaction is more favorite (approximately six times) than the initial reaction step leading to the formation of the first amide bond, as calculated from the mass balance in (a).

It has been observed that the production of heat proceeds even after the addition of TPC ceases. The time needed to the reaction for coming to the end depends on many factors, among which the reactivity of the individual intermediates, the number of bonds formed and the transfer rate of reagents and products in a biphasic system. In fact, the addition rates—along with the stirring rates—control the diffusion of reagents and represent a main rate determining factor of the oligomerization reaction.

3.4. Molar ratio of reagents ([PDA]/[TPC])

Every change in the concentration and initial molar ratio of reagents leads to the formation of oligomers with different average molecular masses and modified distribution of $-\text{NH}_2$ and $-\text{COOH}$ end groups. The factors taken into account are then able to affect not only the nature of the product, but also the reaction mechanism.

An interesting relationship links the ratio [PDA]/[TPC] to either the molecular mass and the distribution of end

groups (Fig. 7a and b); a high [PDA]/[TPC] ratio leads to oligomers with a low \overline{MM} and a predominance of amino end groups, whereas a higher concentration of TPC (with respect to PDA) gives a prevalence of carboxyl end groups in the OPTA, of higher \overline{MM} .

The above relationship turns out to be different from that observed when samples of OPTA are obtained by varying the temperature (Fig. 2a and b). As already pointed out (vide infra), a relatively low temperature gives a prevailing concentration of amino end groups in oligomers of high \overline{MM} or vice versa if temperature is raised, i.e., more $-\text{COOH}$ in low \overline{MM} oligomers.

These results are of practical significance, since an appropriate choice of some experimental conditions (such as temperature and relative concentration of both reagents) allows the polycondensation reaction to be directed towards OPTA products where definite values of either the \overline{MM} or the distribution of end groups can be obtained.

4. Conclusions

The synthesis of aromatic polyamides was carried out in a reaction calorimeter, by low temperature interfacial polycondensation; the evolved heat was measured as a function of several reaction parameters (temperature, time, stirring and addition rates of reagents). The structure of the oligomers synthesized, their average molecular mass and the amino and carboxylic end groups distribution have been related to the reaction parameters described above.

The diffusion of reagents—associated with the addition rate, the stirring and the transfer of reagents from their immiscible solutions—seems to be the main rate determining factor of the process; all these factors in turn influence both the heat evolution and the yields of OPTA. As a result, the overall reaction sequence relies upon a complex interaction of the experimental parameters involved. The initial fast formation of a product with three aromatic rings is followed by the building up of compounds where a stepwise extension of the chains takes place, rather than a further condensation between the three rings compounds.

Moreover, reaction temperature and molar ratio [PDA]/[TPC] are also essential to modify the structure of OPTA and its degree of oligomerization. At relatively high temperature, oligomers characterized by low average molecular mass and high distribution of carboxylic end groups were obtained; at low temperature, oligomers with inverted characteristics were synthesized. Conversely, an high [PDA]/[TPC] ratio leads to low \overline{MM} oligomers with a predominance of amino end groups, whereas an higher concentration of TPC leads the carboxyl groups to prevail in OPTA of high \overline{MM} .

The above results can be rationalized in terms of a different kinetic influence of the reaction temperature on the rates of the competitive processes occurring in the reaction medium, i.e., the formation of amide bonds versus the hydrolysis of terephthaloyl chloride.

Acknowledgements

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