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Polyarylates: thermal stability in air

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Polyarylates were synthesized by the acidolysis of the diacetates of dihydric phenols with diacids using a melt-polymerization technique. These polymers were characterized by solution viscosity, number-average molecular weight and IR spectra. Thermal stability of these polyarylates were studied by dynamic TG in the presence of air. Relative thermal stabilities were compared at the 50% mass loss of a given polymer (T_h value). The data presented revealed that there is a definite relationship between the structure of a polymer chain and their thermo-oxidative stability. The T_h values of some of these polyesters were found to be higher than those reported for highly stable fluoro-carbon polymers (e.g. PTFE). It was observed that the polymers with more cyclic structures in a chain tend to be stiffer and more resistant to deformation. A chain backbone consisting of large number of aromatic groups induced chain stiffening because of chain inflexibility, resonance effects and steric effects.

1. Introduction

Polyarlyates belong to a class of linear polyesters derived from dihydric phenols and dicarboxylic acids. Since their discovery by C. A. Bischoff and A. Hendenstrom (1902) who described the first production of polyarylate of oxalic acid by the reaction of diphenyl oxalate with hydroquinone and resorcinol, a number of polyarylates have been synthesized in various combinations of dihydric phenols with different diacids [1–9] and from the hydroxy aromatic acids [10]. Polymers of this category are associated with many valuable properties such as a high softening point, a good dielectric constant, high stability towards the action of chemical reagents, capability of forming strong films, etc. These surpass polycarbonates, in respect to some of the characteristics). Some areas of their potential applications include the fabrication of various parts in instrument-making and machine-building industries, manufacture of relay boxes and casing transmission parts, heat resistant electrical insulators, etc.

Since, in a large number of practical applications, polymeric materials are exposed to heat during their processing such as pressure moulding, extrusion and casting, it is important to investigate the effect of heat on such polymers. Little work has been done in this direction. Davis and Golden [11] studied the pyrolysis of polyarylates prepared from the terephthaloyl chloride and bisphenol-A and from terephthaloyl chloride and phenolphthalein. Ehlers *et al.* [12] studied the thermal decomposition of poly(*p*-phenylene isophthalate-co-terephthalate), the polymer from 4,4′-dihydroxydiphenyl-methane and isophthalic acid and the polymer from 4,4′-dihydroxydiphenyl ether and 5-amyloxy isophthalic acid in vacuo. They also proposed a possible mechanism of thermal degradation. Thermal degradation of aromatic and semi-aromatic polyesters were also studied by Goldfarb and McGuchan [13]. These workers tried to correlate the thermal stability of polyarylates with their structure.

In the present communication, we report the thermal stability of some polyarylates at higher temperatures (in air) and its correlation with their chemical structure.

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2. Experimental details

2.1. Materials

Sebacic acid and adipic acid (both BDH grade) were recrystallized from hot water and concentrated HNO_3, respectively, whereas isophthalic and terephthalic acid (SISCO Chemicals) were used without purification, hydroquinone (BDH Grade) and bisphenol-A (Sarabhai-MERK) were recrystallized from hot water and toluene, respectively. Catechol and resorcinol were purified by dry distillation. Magnesium ribbon having an oxide layer was cut into smal chips and used as catalyst.

2.2. Preparation of diacetate and diacid chloride

Diacetates of phenols were prepared by acetylation of the corresponding phenol with acetic anhydride in presence of AR H_2SO_4 [14]. *p*-phenylene diacetate was recrystallized from 50% ethanol (mp 122° C) whereas 4,4′-isopropylidenediphenylene diacetate was recrystallized from petroleum ether of 60 to 80° C boiling range (mp 89° C). *o*-phenylene diacetate was purified by dry distillation (mp 69° C).

Terephthaloyl chloride was prepared [15] from terephthalic acid and thionyl chloride and purified by recrystallization from hexane (mp 81° C).

2.3. Preparation of polyarylates

Except for terephthalate polymers, all polyarylates were synthesized using a melt-polymerization technique [16] in the presence of magnesium oxide supported magnesium as a catalyst. An equimolar mixture of 0.05 M diacid and 0.05 M diacetate along with 0.2 g. Mg/MgO was heated in a reaction flask in a nitrogen atmosphere. The initial temperature was 200° C. The mixture became homogeneous upon melting and acetic acid vapours evolved vigorously. After the initial cooking period of two hours the temperature was raised to 250° C and heating was continued for another 10 to 12 h. The product was isolated as a light brown tough solid. The powdered solid was treated with dilute HCl and then washed repeatedly with distilled water. Finally it was washed with ethanol. In this manner, poly(arylene adipates), poly(arylene sebacate) and poly(arylene isophthalates) were synthesized.

For preparing poly(arylene terephthalates), an interfacial-polycondensation technique [14] was used. A solution of 0.025 M terephthaloyl chloride in 75 ml chloroform was added to a well-agitated ice-cooled aqueous solution of 0.025 M phenol in 0.05 M NaOH. The contents were agitated for five minutes and poured into an excess of acetone and filtered. The granular product was washed several times with distilled water to remove the NaCl formed as a by-product. Finally the polymer was washed with acetone and dried.

2.4. Purification of polymer

Except for poly(1,4-phenylene isophthalate) and poly(1,3-phenylene terephthalate) which were insoluble in common organic solvents, all polyarylates were purified by precipitation from their chloroform solutions by the addition of an excess of methanol as a precipitant.

2.5. Thermogravimetric analysis (TGA)

TGA measurements were made with a thermoanalyser supplied by the P and D division, Fertilizer Corporation of India, Sindri (India). A Pt–Pt/Rh thermocouple with a temperature range 20 to 1400° C was used as a temperature indicator. All the measurements were made at a linear heating rate of $5^\circ C\,min^{-1}$ in air. An accurately weighed dried polymer powder (100 mg) in a platinum crucible was hung in the furnace and the residual mass was recorded at a regular interval of 20° C until the mass loss was complete. TG curves were obtained on plotting the residual mass as a function of temperature.

3. Results and discussion

The physical characteristics of the various polyarylates are summarized in Table I.

For obtaining the relative thermal stabilities of polyarylates, the method described by Madorsky [17] was adopted. According to him, the temperature corresponding to 50% mass loss of a given polymer, designated as the half-decomposition temperature (T_h value) can be taken as an index while predicting its relative thermal stability. TG curves of polyarylates are shown in Fig. 1. The T_h values for different polyarylates are recorded in Table II in a descending order of magnitude. The same is the order of their relative thermal stabilities.

A closed outlook at Table II reveals that there exists a definite relationship between the structure of the polymer chain and its thermo-oxidative stability. Among the polyarylates studied so far, poly(4,4′-isopropylidenediphenylene terephthalate) was found to be the most stable one. This was

TABLE I Physical characteristics of various polyarylates

Polymer	Solvents	Melting temperature, (°C)	Number-average molecular weight $\bar{M}_n$	Solution viscosity (30°C) ($cm^3 gm^{-1}$)	Other properties
1. Poly(1,4-phenylene sebacate)	Chloroform, methylene chloride, *m*-cresol	167–172	2400	$[\eta]$, 40 (chloroform) η_{inh}, 21 (*m*-cresol)	Capable of being melt-pressed, forms brittle and opaque films
2. Poly(1,4-phenylene adipate)	Chloroform, *m*-cresol, hot *o*-dichlorobenzene, phenol-chlorobenzene mix. (1:1, wt%), nitrobenzene-phenol mix. (1:1, wt%)	198–205	3300	$[\eta]$, 42 (chloroform) η_{inh}, 29 (*m*-cresol)	Capable of being melt-pressed, forms brittle and opaque films
3. Poly(1,2-phenylene isophthalate)	Benzyl alcohol, chloroform, *o*-dichlorobenzene, Trichloroethylene, THF	115–121	2320	$[\eta]$, 16 (chloroform) η_{inh}, 12 (trichloroethylene)	Long fibres could be pulled out from melt
4. Poly(1,4-phenylene isophthalate)	Insoluble in common organic solvents, soluble in benzophenone at elevated temperature, also soluble in AR H_2SO_4	Infusible	–	–	–
5. Poly(1,3-phenylene terephthalate)	Insoluble in common organic solvents	Infusible	–	–	–
6. Poly(4,4′-isopropylidenediphenylene adipate)	Chloroform, *m*-cresol, phenol-chlorobenzene mix. (1:1, wt%), THF acetone, Trichloroethylene	75–81	1100	$[\eta]$, 11 (chloroform) η_{inh}, 9 (Trichloroethylene)	Polymer appeared to be purely amorphous.
7. Poly(4,4′-isopropylidenediphenylene isophthalate)	Chloroform, *m*-cresol, phenol-chloro-benzene mix. (1:, wt%), sym-chloroethane-phenol mix.	258–270	4000	$[\eta]$, 19 (chloroform) η_{inh}, 24 (phenol-chlorobenzene mix. 1:1, wt%)	The polymer was capable of being melt pressed and formed transparent film. Long fibres could be drawn from the melt.
8. Poly(4,4′-isopropylidenediphenylene terephthalate)	Chloroform, sym-tetrachloroethane-phenol-mix. (1:1, wt%) phenol-chlorobenzene mix. (1:1, wt%)	High melting temperature above 300°C	–	$[\eta]$, 21 (chloroform) η_{inh}, 24 (phenol-chlorobenzene mix. 1:1, wt%)	–

*$\bar{M}_n$ were obtained from end-group analysis of carboxyl end-groups by titration method [18].

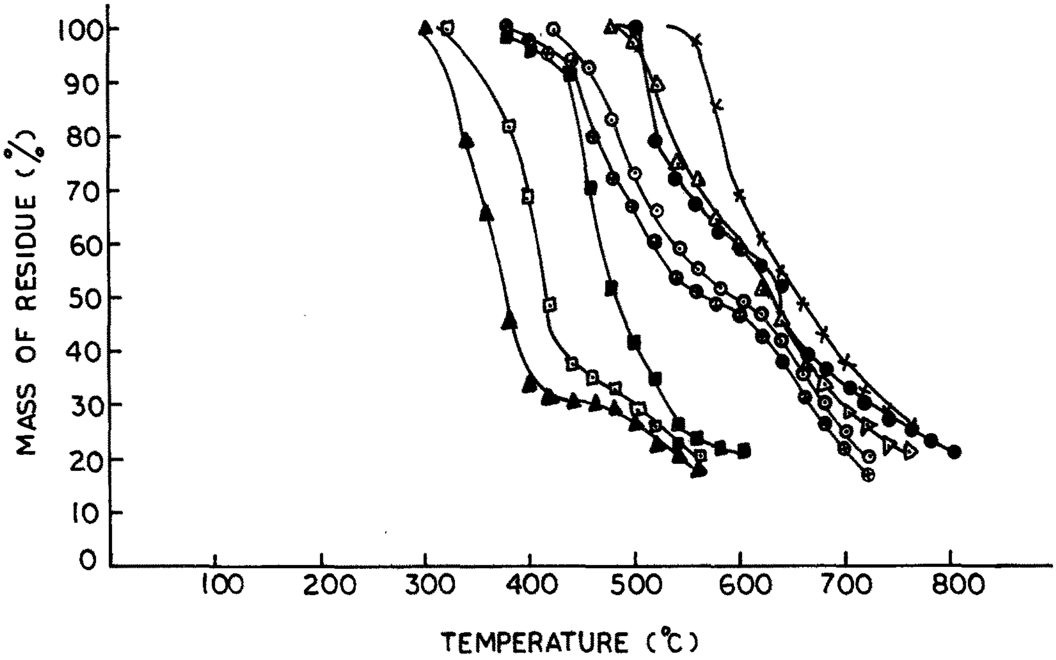


Figure 1 Relative thermal stability of polyarylene esters. ▲ poly(1,4-phenylene adipate). □ poly(4,4′-isopropylidene diphenylene adipate). ■ poly(1,4-phenylene sebacate). ⊖ poly(1,2-phenylene isophthalate). ○ poly(1,3-phenylene terephthalate). △ poly(1,4-phenylene isophthalate). ● poly(4,4′-isopropylidene diphenylene isophthalate). X poly(4,4′-isopropylidene diphenylene terephthalate).

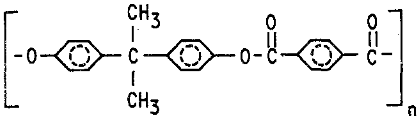
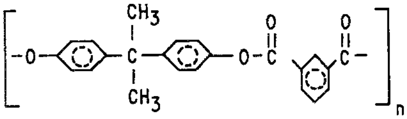
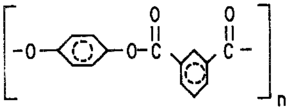
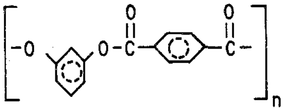
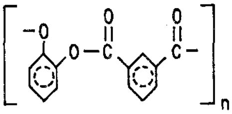
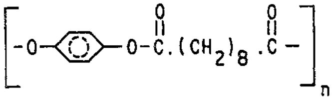
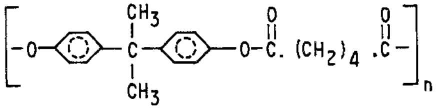
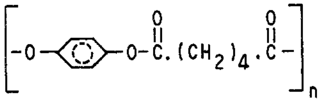
possibly due to the presence of a large number of phenylene rings in the polymer backbone (three benzene rings per repeat unit) all in *para* positions. The enhanced stability was attributed due to resonance which was introduced in the chain by these aromatic rings. It was interesting to note that the T_h value of this polymer was higher than those reported for a highly stable fluorocarbon polymer, i.e. poly(tetrafluoro ethylene) by Madorsky [17] (T_h value 487° C for heating in air at 300 mm pressure; and 509° C for heating in vacuum). It is an obvious fact that polymers with more cyclic structures in their chains tend to be stiffer and more resistant to deformation. A chain backbone consisting of a large number of aromatic groups induces chain-stiffening because of chain inflexibility, resonance effects (which are enhanced by coplanarity), steric factors, etc.

Similarly, poly(1,4-phenylene isophthalate) appeared to be less stable than poly(4,4′-isopropylidenediphenylene isophthalate) as the former contained two aromatic rings (i.e. a chain stiffening group) per chain whereas the latter contained three benzene rings per repeat unit (imparting towards its enhanced thermal stability).

The type of aromatic substitution also played an important role in affecting the thermal stability of polyarylates which was possibly due to a combination of various factors, e.g. resonance, steric factors, etc. Thus poly(4,4′-isopropylidenediphenylene terephthalate), containing all *p*-substituted aromatic rings, was more stable than poly(4,4′-isopropylidenediphenylene isophthalate) which contained *m*-substituted phenylene rings in addition to *para*-rings as a component of their polymer backbone. Similarly, poly(1,3-phenylene terephthalate), a polymer derived from 1,3-dihydroxybenzene, was more stable than poly(1,2-phenylene isophthalate) which was derived from 1,2-dihydroxybenzene. But, the former was less stable than poly(1,4-phenylene isophthalate), a polymer obtained from 1,4-dihydroxybenzene. It appeared that the effect of isomeric substitution in the phenolic moeity was more important than the substitution effect in the acid component while predicting the thermal stability.

Semi-aromatic polyesters (i.e. polyesters derived from aliphatic acids) were comparably less thermally stable than all aromatic polyesters as they possessed enhanced chain flexibility and reduced chain stiffness resulting in lower thermal stability. Furthermore, aliphatic moeities provided

TABLE II Relative thermal stabilities of polyarylates (based on temperature of half-decomposition)

Polymer	Polymer structure	T_h(°C)
Poly(4,4′-isopropylidenediphenylene terephthalate)		655
Poly(4,4′-isopropylidenediphenylene isophthalate)		640
Poly(1,4-phenylene isophthalate)		630
Poly(1,3-phenylene terephthalate)		595
Poly(1,2-phenylene isophthalate)		565
Poly(1,4-phenylene sebacate)		470
Poly(4,4′-isopropylidenediphenylene adipate)		420
Poly(1,4-phenylene adipate)		380

hydrogen atoms which can undergo thermal, oxidative and chemical reactions more readily.

Poly(1,4-phenylene sebacate) appeared to be more stable than poly(1,4-phenylene adipate) as the former contained low oxygen content (23.2%) than the latter (30.8%). Poly(4.4′-isopropylidenediphenylene adipate) was found to be less stable than poly(1,4-phenylene adipate). The lower stability of the former was possibly due to its very low melting temperature (78°C) and lower molecular weight as compared with the latter (Table I).

Thus, it was finally concluded that the structure of polymer backbone played a key role in imparting its thermal stability. Molecular weight, melting temperature, oxygen content, etc. were the other factors which play a supplementary role in establishing the thermal stability of polyarylates.

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