THERMAL PROPERTIES OF ARAMID–POLYDIMETHYLSILOXANE BLOCK COPOLYMERS

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ABSTRACT

The thermal properties of the aramid-polydimethylsiloxane block copolymers constituting various types of aramids and polydimethylsiloxane with different molecular weights have been studied by thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) both in air and nitrogen atmospheres. In general, these block copolymers displayed excellent thermal properties even in those cases where products with low degree of polymerization were prepared. These block copolymers showed an optimized range of temperature of decomposition >400°C irrespective of having aramid block as terephthalamide or isophthalamide. But in aramid as parent polymer, the temperature of decomoposition strongly depends on the orientation of the constituting aromatic rings i.e., terephthalamide or isophthalamide and it specifies the use of aramids as heat resistant materials.

INTRODUCTION

The ever-increasing need for thermally stable polymers is constantly creating a demand for more information on the thermal properties of such materials. While much thermodynamic data is available on single compounds but reliable information is relatively scarce on high molecular weight polymeric materials. One of the important measurements of polymers to determine in order to know how successfully they may be used at elevated temperatures is TGA. The TGA behavior of the polymer in air and nitrogen atmosphere is to determine the temperature at which pyrolytic decompositions become rapid.

Aramids are characterized as the oldest high temperature resistant materials with a favorable balance of other physical and chemical properties.(1) On the other hand the multiphase polymers of polydimethylsiloxane such as block and graft copolymers are known to exhibit unique properties such as high thermal and oxidative stability, low temperature surface activity, flexibility and biocompatibility. On the basis of these properties block copolymers of polydimethylsiloxane have numerous industrial and medical applications where these properties play a major role. By chemical manipulation of the silicon substituents organo functional siloxanes containing relevant arm functionality have been prepared and utilized for which the parent polymer is unsuitable.(2-5) These hard-soft block copolymers are expected to exhibit optimum properties which make them suitable for many applications. We were therefore motivated to synthesize these materials by copolymerization of aramids with polydimethylsiloxane. The block copolymers of the $[(A)_x(B)_y]_n$ type, $[(\text{aramid})_x(\text{polydimethlsiloxane})_y]_n$ were synthesized by polycondensation of aramid and linear amino propyl terminated polydimethylsiloxane oligomers of different molecular weight. (6)

This paper summarizes our investigations of thermal behavior and stability with particular emphasis on the structure of the aramid in these block copolymers.

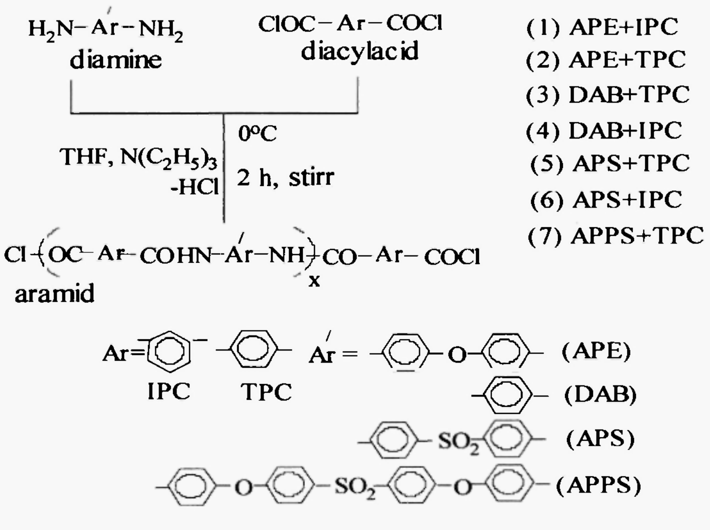
EXPERIMENTAL

Measurements

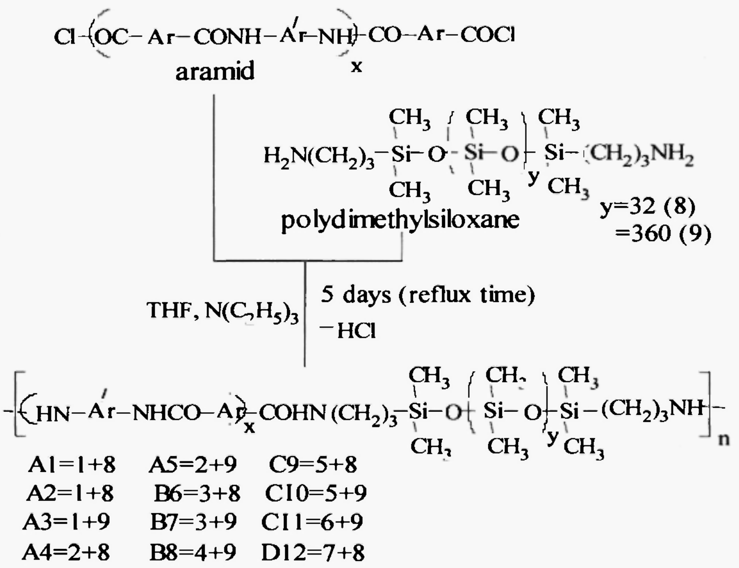
The thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis(DTA) were carried out on NETZSCH Simultaneous Thermal Analyzer 409 thermobalance using air and nitrogen atmospheres at heating rate of 10°Cmin^{-1} to a temperature of 1000°C.

RESULTS AND DISCUSSION

The aramid-polydimethylsiloxane block copolymers synthesized (6) consists of four groups as shown in fig 1. The polydimethylsiloxanes possessing good thermal oxidative stabilities and very good resistance against atomic oxygen degradation, depolymerize near 400°C(7)



Scheme. I Synthesis of aramids.



Scheme II Synthesis of block copolymers.

Fig 1: Synthesized aramid-polydimethylsiloxane block copolymers scheme I and II.(6)

The aramids, because of intermolecular bonding and chain stiffness, possess high thermal stability. (8-10) The decomposition temperatures (10% weight loss) of the aramids (used in these block copolymer synthesis) are literature values reported in table I. (11-14) The decomposition temperature depends upon the type of the aramids i.e., the structure of isophthalamide and terephthalamide determine the chemical and physical properties of the aramids. The para-para orientation of aromatic rings in terephthalamide makes it thermally more stable than the isophthalamide with meta-meta orientation. The decomposition temperatures (10% weight loss) of the aramid-polydimethylsiloxane block copolymers are reported in table II with an optimized range from 408to 467°C both in air and nitrogen atmosphere.

Table I: 10% weight loss temperature of aramids recorded by thermogravimetric analysis.

Aramid-polydimethylsiloxane block copolymers	Aramid block		Decomposition temperature °C in		Ref no
	diamine	diacidchloride	nitrogen	air	
A1--A3	APE	IPC	465	450	(10)
A4--A5	APE	TPC	568	-	(11)
B6--B7	DAB	TPC	550	545	(10)
B8	DAB	IPC	495	480	(12)
C9--C10	APS	TPC	-	-	
C11	APS	IPC	-	-	
D12	APPS	TPC	510	500	(13)

Isophthaloylchloride (IPC), terephthaloylchloride (TPC), 4,4′-bis(aminophenyl)ether (APE), 1,4-diaminobenzene (DAB), 4,4′-bis(aminophenyl)sulfone (APS), 4,4′-bis (3-aminophenoxy diphenyl)sulfone (APPS), polydimethylsiloxane (PDMS).

The thermogram curves for block copolymers in controlled atmospheres are shown in figs 2a,b-5a,b. In all cases, the curves in air and nitrogen atmospheres show no point of inflection, which indicates the existence of one stage in the overall decomposition process. In all the recorded thermograms the temperature at which thermal depolymerization commences is greater than 400°C, confirms the stability of polydimethylsiloxane phase in these copolymers.

Owing to the presence of the polar amide linkage, the polyamide absorb significant amount of moisture and the TGA curves show a small weight loss in the range 45-125°C, due to water desorption(15) But in these block copolymers it has not been observed due to synthesis in inert atmosphere and hydrophobic behavior of polydimethylsiloxane phase in these copolymers.

Table II: 10% weight loss temperature of block copolymers observed by TGA at a heating rate of 10°Cmin^{-1}.

Aramid-polydimethylsiloxane block copolymers	Aramid block	PDMS block	Block copolymers	Decomposition temperature °C in atmosphere		Maximum weight loss temperature °C from DTG in atmosphere	
	x	y	n	nitrogen	air	nitrogen	air
A1	8	32	6.3	456	412	487	-
[a] A2	11	32	1.5	453	423	503	-
A3	16	360	2.8	456	436	514	501
A4	3	32	8.1	456	417	501	456
A5	20	360	1.5	467	408	512	487
B6	3	32	4.4	446	418	514	458
B7	13	360	1.5	460	417	518	457
B8	18	360	1.9	460	432	492	494
[b] C9	20	32	-	412	410	-	-
[b] C10	100	360	-	438	422	474	463
[b] C11	425	360	-	442	423	473	-
D12	3	32	4.7	434	431	434	431

[x] Degree of polymerization of aramid. [y] Degree of polymerization of PDMS. [n] Degree of polymerization of block copolymers. [a]Rout of synthesis was different from all other block copolymers. [b]Too insoluble for GPC measurements, degree of polymerization found from NMR.(6)

The TGA results of block copolymers when compared to their parent polymer i.e., aramids, it was found that the decomposition temperature did not depend upon the structure of the aramid block, although as parent polymer thermal stability strongly depends upon the structure of the aramid. (11-14) The block copolymers also possess some new properties along with the properties of their parent polymers. So an optimized range for temperature of decomposition in all these block copolymers have been observed irrespective of aramid as terephthalamide or isophthalamide.

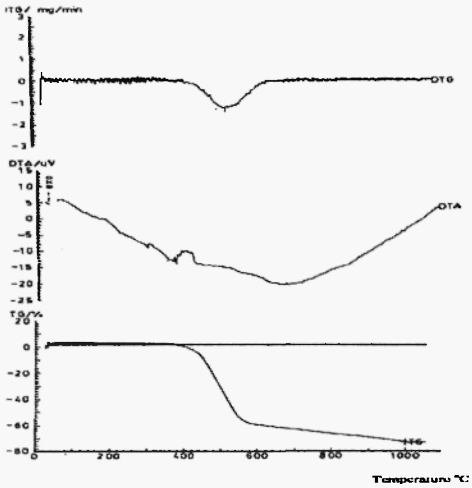


Fig. 2a: TGA, DTA and DTG curves of a typical A block copolymer (A1) under N_2.

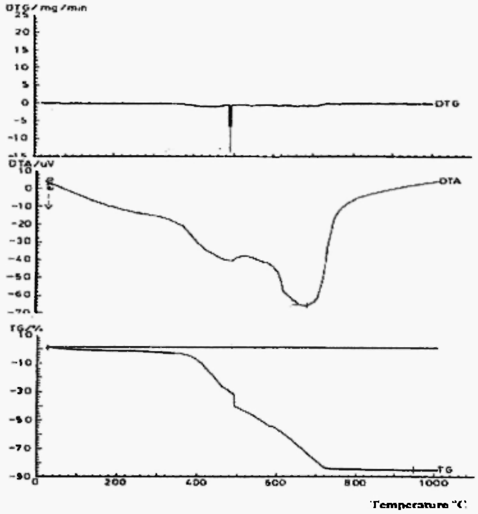


Fig. 2b: TGA, DTA and DTG curves of a typical A block copolymer (A1) under Air

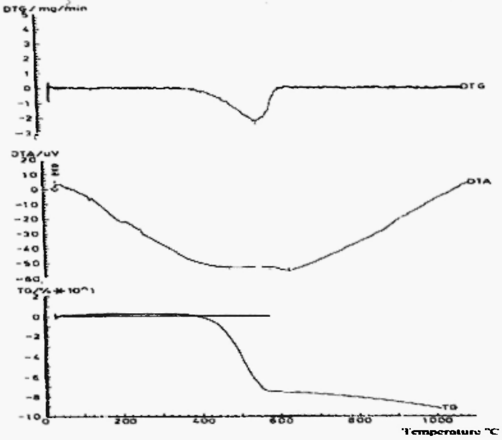


Fig 3a: TGA, DTA and DTG curves of a typical B block copolymer (B6) under N_2

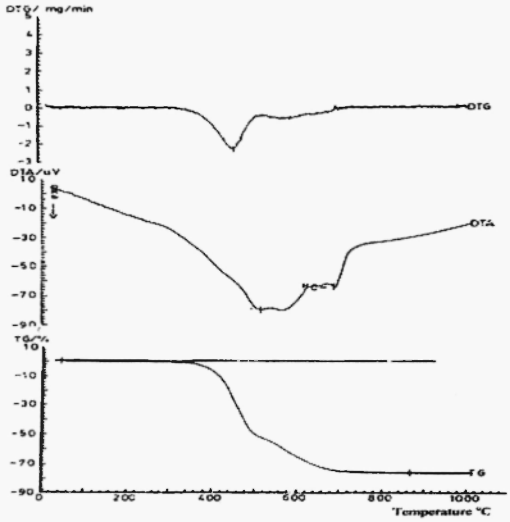


Fig 3b: TGA, DTA and DTG curves of a typical B block copolymer (B6) under A

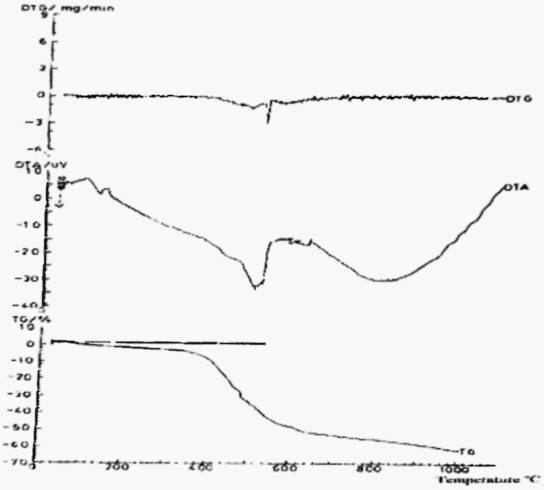


Fig. 4a: TGA, DTA and DTG curves of a typical C block copolymer (C9) under N_2

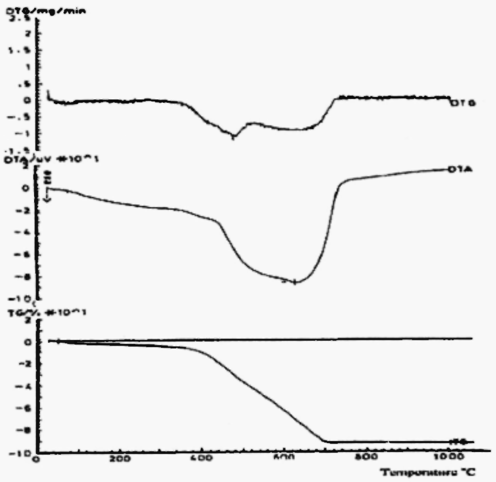


Fig. 4b: TGA, DTA and DTG curves of a typical C block copolymer (C9) under air

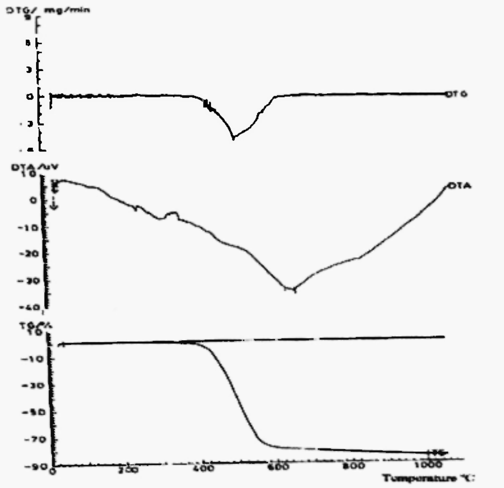


Fig. 5a: TGA, DTA and DTG curves of a typical D block copolymer (D12) under N_2

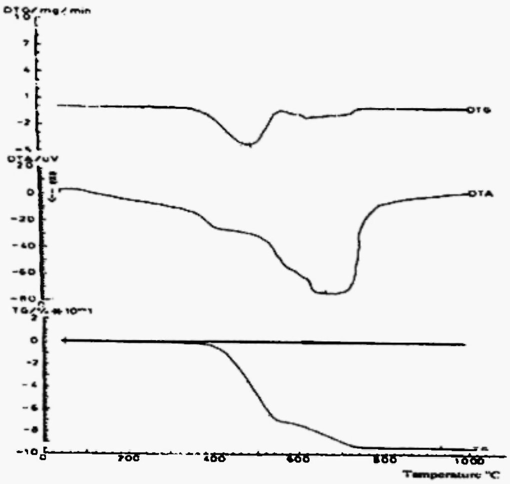


Fig. 5b: TGA, DTA and DTG curves of a typical D block copolymer (D12) under air

The DTA of aromatic polyamides show endothermic peaks at higher temperature(16) i..e., the thermal stability of these materials due to amide linkages along with aromatic structures. On the other hand endothermic peak for polydimethylsiloxane is observed at low temperatures due to siloxane backbone structural conformation.(17) But all the block copolymers showed endothermic peaks at low as well as at high temperature(6) i.e., the aramid character was dominant in all these copolymers at high and polydimethylsiloxane at low temperature. The excellent phase separation in these block copolymers has also been confirmed by DSC, NMR, FTIR.(6)

CONCLUSION

TGA measurements suggested that the synthesized aramid-polydimethylsiloxane block copolymers showed an optimized range for temperature of decomposition irrespective of having aramid block as terephthalamide or isophthalamide, which is a new thermal property attributed to the structure of these block copolymers.

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