Homo - and Copolyimides From 2,3,3',4'-Biphenyltetracarboxylic Dianhydride

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Introduction

Since the beginning of high performance/high temperature polymer developmennt more than 40 years ago, attention has focused on polyimides moreso than any other polymer family. This was primarily due to the availability of monomers (particularly aromatic dianhydrides and diamines), the ease of polyimide synthesis, and their unique combination of physical and mechanical properties (1-3). A significant amount of technology was developed such that polyimides are widely used as adhesives, coatings, composite matrices, fibers, films, foams, membranes, and moldings in many industries ranging from communications to medicine to transportation. The estimated market for polyimides in 2000, excluding polyetherimides, was $1.065 Billion (4).

Over the years, many different polyimides have been made from various synthetic routes. The most popular route is the reaction of an aromatic diamine with an aromatic dianhydride to form a soluble precursor polyamide acid (amic acid) that is subsequently converted chemically or thermally to the polyimide. Many different aromatic diamines and aromatic dianhydrides have been used to prepare polyimides. From this work, structure/property relationships have been established that can be used to design polyimides for particular applications. New aromatic dianhydrides and aromatic diamines continue to evolve. An interesting aromatic dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA), was reported in 1973 (5) and recently used to prepare linear homo- and copolyimides (6-11). Polyimides from a-BPDA exhibit higher glass transition temperatures and more thermoplasticity than the analogous polyimides from 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) (8b).

As part of an effort at NASA Langley to develop materials for space applications that require a unique combination of properties such as thin films for antennas, concentrators, solar sails, coatings on second-surface mirrors, thermal/optical coatings, and multi-layer insulation blanket materials, work has concentrated on polyimides. Recently a series of homo- and copolyimides based upon a-BPDA have been prepared. The chemistry and properties of these polymers will be discussed.

Results and Discussion

Several polyimides were prepared from the reaction of a-BPDA with aromatic diamines via of the precursor polyamide acid or directly to the polyimide by reaction in hot m-cresol. The properties of the polymers and their thin films are presented in Tables 1-5. The last 2 polymers in Tables 1-4 were made from a-BPDA and s-BPDA to provide a comparison between the asymmetric and symmetric catenated polymers. In virtually all cases, the a-BPDA derived films had higher Tgs, less color, and lower tensile properties than the s-BPDA based films. In Table 5, the properties of a-BPDA based films cured at 250, 300, and 350°C are presented. The Tg increased, the color darkened, and mixed changes occurred in the tensile properties as the film cure temperature was raised.

Copolyimides were prepared via the polyamide acids from the reaction of various amounts of a-BPDA and pyromellitic dianhydride (PMDA) with 4,4'-oxydianiline (4,4'-ODA) in N,N-dimethylacetamide (DMAC). Initially the polyamide acid solutions were stirred under nitrogen at ambient temperature for 5-6 hours. Thin films were cast on plate glass, placed in a dry air chamber for 16 hours, and subsequently converted to the polyimide by stage-heating to 300°C for 1 hour. As presented in Table 6, the molar ratio of a-BPDA to PMDA was 9:1, 7:3, 1:1, 3:7, and 1:9. Films from the 7:3, 1:1, and 3:7 molar ratio polymers shattered during the cure. Different curing cycles failed to provide good films. Because of the difference in the reactivity of PMDA and a-BPDA, block domains were apparently formed where the two blocks were incompatible. Hence, in thermally converting the polyamide acid film to polyimide, cracking occurred. When the polyamide acid solutions were strirred for 24 hours, equilibration apparently took place to randomize the polyamide acids. This occurs because of the equilibrium between the polyamide acid and the anhydride/amine (12). Transparent, yellow, fingernail creaseable films from the 7:3, 1:1, and 3:7 molar ratio polyimides were cast from the polyamide acid solutions stirred for 24 hours. Properties are shown in Table 6.

In these copolyimides, the mode of addition of the dianhydrides to the diamine was also studied. PMDA (0.5 mole %) was added to the diamine (1.0 mole %) solution and subsequently stirred at ambient temperature for 24 hours. The other dianhydride, a-BPDA (0.5 mole %), was added and the solution was stirred for 6 hours. A film was cast that shattered upon stage-curing to 300°C. This was performed with the anticipation that a more random copolymer would be formed. When the final polyamide acid solution was stirred for 24 hours instead of 6 hours, the polyamide acid solution provided a transparent, yellow, fingernail creaseable film. The opposite addition (a-BPDA first) provided the same results.

Although the differential scanning calorimetric curves of many of the copolymers showed an intense endothermic peak in the initial run such as that in Figure 1, all of the films were amorphous as shown by wide angle x-ray diffraction measurements. Upon reheating the samples after quenching at 400°C, transitions characteristic of Tgs were observed. Some of the shattered films and one that simply sustained large cracks during the curing process exhibited two Tg transitions, suggesting block copolymers. The lower Tgs were significantly less than the Tg (314°C) of the a-BPDA/4,4'-ODA polymer. The reported Tg of the a-BPDA/4,4'-ODA polymer was 340°C (6). Films cast from the polyamide acid solutions that were stirred at ambient temperature for 24 hours had single Tgs, indicating random copolymers.

Acknowledgement

The authors greatly appreciate a generous sample of a-BPDA from Ube Industries, Inc.

References

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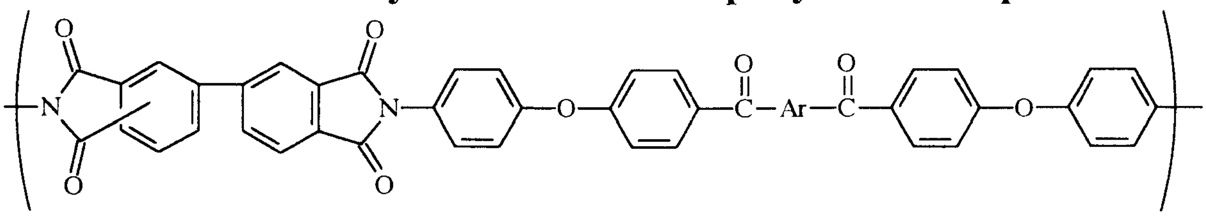
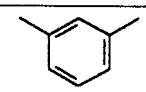
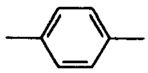
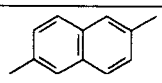
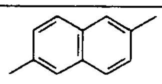
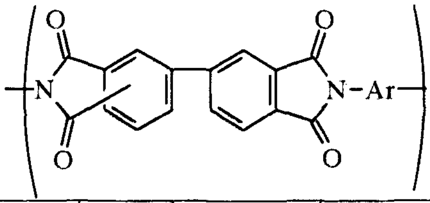
Table 1 - Polyimide Structure/Property Relationship

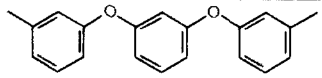
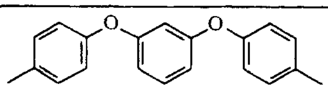
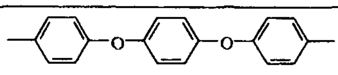
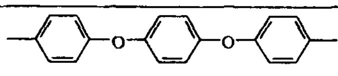


Dianhydride	Ar	η_{inh}, dL/g PAA	Tg (Tm), °C Film[1]	Film Color	23°C Tensile Properties Strength, MPa	Modulus, GPa	Elong, %
asym		1.21	237	Yellow	95	2.6	11
asym		1.08	256	Yellow	92	2.5	10
asym		0.95	263	Light orange	99	2.4	9
sym		1.19	252 (417)	Orange, opaque	112	2.4	3

Made via the polyamide acids
1. Film cured for 1 hour at 250°C

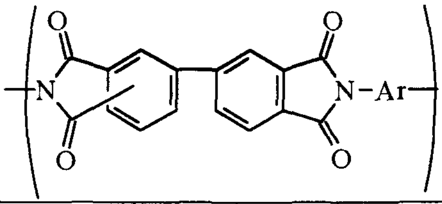
Table 2 - Polyimide Structure/Property Relationship

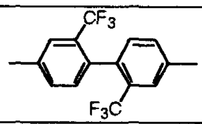
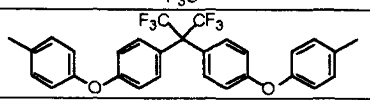
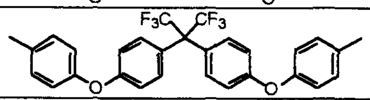


Dianhydride	Ar	η_{inh}, dL/g PAA	Tg (Tm), °C Film[1]	Film Color	23°C Tensile Properties		
					Strength, **MPa**	Modulus, **GPa**	Elong, %
asym		0.73	207	Near colorless	110	3.0	6
asym		1.51	248	Light yellow	80	2.5	5
asym		1.44	276[2]	Pale yellow	99	2.4	9
sym		2.20	265[2] (455)	Yellow	143	4.1	34

Made via the polyamide acids
1. Film cured for 1 hour at 250°C
2. Film cured for 1 hour at 300°C

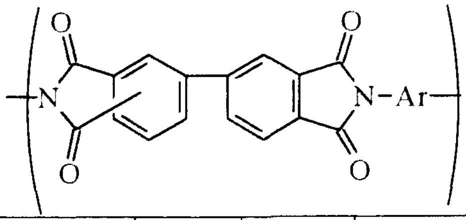
Table 3 - Polyimide Structure/Property Relationship

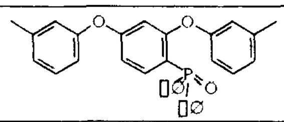
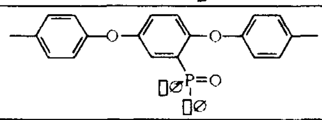
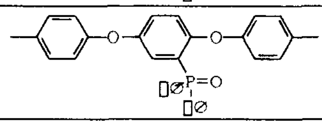


Dianhydride	Ar	η_{inh}, dL/g PAA	Tg, °C Film[1]	Film **Color**	23°C Tensile Properties		
					Strength, MPa	Modulus, GPa	Elong, %
asym		0.83[2] imide	329[3]	Orange	111	3.1	5
asym		1.14	261	Pale Yellow	124	3.0	7
sym		1.93	254	Yellow	111	3.0	31

Made via the polyamide acid
1. Film cured for 1 hour at 250°C
2. Made in m-cresol
3. Film cured for 1 hour at 350°C

Table 4 - Polyimide Structure/Property Relationship



Dianhydride	Ar	η_{inh}, dL/g	Tg, °C Film[3]	Film Color	23°C Tensile Properties		
					Strength, MPa	Modulus, GPa	Elong, %
asym[1]		0.55 imide	233	Near colorless	73	3.5	23
asym[2]		0.50	250	Orange	112	3.4	5
		0.59	259[4]	Orange	109	3.4	13
sym[2]		0.75	245	Orange	129	3.7	10
		1.00	258[4]	Orange	151	4.3	31

1. Made in m-cresol
2. Made via the polyamide acid
3. Films cured for 1 hour at 250°C
4. Films cured for 1 hour at 300°C

Table 5 - Properties of a-BPDA Polymers and Films Cured at Different Temperatures

Diamine	η_{inh}, dL/g PAA	Cure Temp. for 1 hour, °C[1]	Tg, °C (Film)	Film Color	Transmission at 500 nm, % (Film thickness, mm)	23°C Tensile Properties		
						Strength, MPa	Modulus, GPa	Elong., %
1,3,3-APB[2]	0.65	250	204	Near colorless	87 (0.066)	108	3.3	4
		300	207	Pale yellow	85 (0.048)	114	3.1	5
		350	209	Yellow	69 (0.058)	124	3.3	6
	0.66	250	202	Near colorless	86 (0.058)	106	3.0	5
		300	207	Pale yellow	82 (0.064)	119	3.1	5
		350	208	Yellow	70 (0.062)	120	3.2	6
1,4,4-APB[3]	1.47	250	276	Pale yellow	85 (0.046)	103	2.7	7
		300	278	Yellow	84 (0.046)	97	2.6	22
		350	287	Light orange	66 (0.043)	94	2.3	44
	1.49	250	278	Pale yellow	85 (0.046)	108	2.7	8
		300	279	Yellow	82 (0.041)	106	2.7	13
		350	285	Yellow	70 (0.043)	103	2.7	17

1. Cure temperatures are accumulative (i.e. 350°C cure is 1 hour each at 250, 300, and 350°C)
2. 1,3-Bis(3-aminophenoxy)benzene
3. 1,4-Bis(4-aminophenoxy)benzene

Table 6 Properties of Homo- and Copolyimides

Dianhydride, molar ratio (diamine 4,4'-ODA)	PAA Rx time, hr	η_{inh}, dL/g	Initial Tg (endo peak), then Tg (endo peak) after 400°C quench, °C	Film**	RT Tensile Properties		
					Strength, MPa	Modulus, GPa	Elong., %
PMDA*	6	0.77	Not detected, ~380	orange, creaseable,	105	2.5	25
a-BPDA*	6	0.92	(291) 315, 314	yellow, creaseable,	101	2.7	6
9:1 PMDA/a-BPDA*	5	0.81	sl. shoulder @ 324, (448)	orange, creaseable	119	3.2	14
7:3 PMDA/a-BPDA*	6	0.73	(326), 251	shattered			
exact stoichiometry	24		ill-defined,				
1:1 PMDA/a-BPDA*	5	0.97	(322), 252 and 329	shattered			
	5	0.81	(333), 248 and 325	shattered			
exact stoichiometry	6	1.00		shattered @ 150°C during cure			
	24	1.17	ill-defined, 343	orange, creaseable	97	2.7	10
	48	1.15	ill-defined, 348	orange, creaseable	93	2.5	15
3:7 PMDA/a-BPDA*	6	0.66	(328), 324	shattered			
exact stoichiometry	24	1.24	(337), 333	orange, creaseable	92	2.4	6
1:9 PMDA/a-BPDA*	6	0.88	(320), 248 and 321	cracked into large pieces, yel., flexible	108	2.6	14

* Molecular weight about 25,000g/mole, endcapped with phthalic anhydride

** All films cured through 1 hr @ 300°C, all films amorphous by WAXD

Fig. 1 - DSC Curves of 70:30 a-BPDA/PMDA/4,4'-ODA Copolyimide