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INVESTIGATION OF THE EFFECTS OF SHORT CHAIN PROCESSING
ADDITIVES ON POLYMERS

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ABSTRACT

The effects of low level concentrations of several short chain processing additives on the properties of the BDSDA/ODA/MPD [422] copolyimide have been investigated. It has been noted that 5 percent MPD/PA is more effective than 5 percent ODA/PA and BDSDA/AN in strengthening the host material. However, the introduction of 10 percent BDSDA/AN produces disproportionately high effects on free volume and free electron density in the host copolyimide.

INTRODUCTION

Physical properties of copolyimides synthesized from linear BDSDA/ODA and BDSDA/MPD homopolymers had been investigated previously, using Positron Annihilation Spectroscopy (PAS)⁽¹⁾. These studies had indicated that the copolyimides have a unique transition molecular structure characterized by higher electron density and stronger bonds, i.e., greater chain-chain interactions. The transition structure permits both physical as well as chemical entry of water molecules in it. Following these discoveries, it was decided to study the effects of several short chain processing additives on the properties of the optimal BDSDA/ODA/MPD [422] copolyimide. The results of these studies are described in the following sections.

LIST OF SYMBOLS

BDSDA	4,4' - bis(3,4 - dicarboxyphenoxy) diphenylsulfide dianhydride
ODA	4,4' - diaminodiphenyl ether
MPD	1,3' - diaminobenzene (m-phenylene diamine)
PA	Phthalic anhydride
AN	Aniline
BDSDA/AN	BDSDA end-capped with aniline
ODA/PA	ODA end-capped with phthalic anhydride
MPD/PA	MPD end-capped with phthalic anhydride
BDSDA/ODA/MPD	Copolyimide containing equal mole fractions of BDSDA/ODA and BDSDA/MPD homopolymers [422]
w/o	Weight percent
τ_1	Lifetime of short lifetime component in the positron spectrum

τ_2	Lifetime of long lifetime component in the positron spectrum
I_2	Intensity of the long lifetime component in the positron annihilation spectrum
Na ²²	Sodium-22 (positron emitting isotope of sodium)
μc	Microcurie - a unit of radioactivity equalling 3.7×10^4 disintegrators/sec

EXPERIMENTAL PROCEDURE AND RESULTS

(a) Preparation of the 422 Copoly(amic acid) Powder⁽²⁾. Sublimed 4,4'-oxydianiline (ODA) (49.08 g, 0.2451 mol) was dissolved under nitrogen in 2-methoxyethyl ether (diglyme) in a flamed 2 L reaction kettle equipped with a mechanical stirrer and lid. 4,4'-bis(3,4-dicarboxyphenoxy) diphenylsulfide dianhydride (BDSDA) (250.0 g, 0.492 mol) was added in one charge, washing traces of the remaining dianhydride into the kettle with the remaining diglyme and requiring a total of 1305 g of this solvent. Stirring was maintained at 300 rpm. After 25 min m-phenylenediamine (MPD) (26.47 g, 0.2448 mol) was added, resulting in the formation of a slurry of stringy solid in a tan solution. The stirring was continued for 18 hours, during which time these suspended particles dissolved and the solution became black and viscous. Phthalic anhydride (PA) (0.7260 g, 0.0049 mol) dissolved in 1.70 g of diglyme was then added and the stirring was increased to 700 rpm for 1 hour. The resulting poly(amic acid) solution at 20 percent solids had an inherent viscosity of 0.61 when run in N,N-dimethylacetamide (DMAC) at 0.5 percent solids solution and 35°C.

Precipitation of this resin was conducted in a large household blender by pouring a slow stream of the base resin solution into the stirred blender two-thirds full of distilled water. The precipitated off-white solid was filtered through cheese cloth, reslurried in distilled water in the blender, refiltered and dried at ambient temperature for 2 days. This solid was further dried for 1 week under vacuum at ambient temperature. The yield of poly(amic acid) powder was 364.5 g (theoretical yield, 326.3 g), indicating that this polymer contained a residual amount of solvent and (or) water. Figure 1 shows molecular structure of the 422 copolyimide.

(b) Preparation of the Di(amic acid) Additives and the 422 Copolyimide Mixtures and Their Conversion to Target Moldings for PAS. As shown in Table I the three di(amic acid) additives were prepared at ambient temperature by reacting the anhydride with the amine in the ratios shown in an equivolume mixture of diglyme and 1-methyl-2-pyrrolidinone (NMP). Thus, BDSDA and aniline (An) were reacted in a 1:2 molar ratio; similarly, phthalic anhydride and ODA (2:1) were converted to the di(amic acid). Phthalic anhydride and MPD (2:1) were also reacted. The resulting amic acid solutions were precipitated with water, and the powders were air dried.

TABLE I. Experimental Summary of Di(amic acid) Additive Synthesis

Anhydride	Amine	Molar Ratio	M.P. (DTA Onset, °C)	Analysis (%)		
				Calculated	Experimental	
BDSDA	AN	1:2	100	C	68.96	68.52
				H	4.05	4.43
				N	4.02	5.34
PA	ODA	2:1	105	C	67.74	70.92
				H	4.06	4.04
				N	5.64	6.44
PA	MPD	2:1	147	C	65.34	64.43
				H	3.99	4.96
				N	6.93	6.03

The 20% solids 422 copoly(amic acid) solution was mixed with the calculated amount of each additive and stirred overnight at ambient temperature. The mixture was then precipitated with water in a blender, air dried, and imidized for 1 hour each at 100°C and 220°C. The resulting powders were then converted to unfilled moldings⁽³⁾ for PAS measurements. The unmodified 422 copoly(amic acid) powder was similarly imidized for comparison.

(c) Measurement of Saturation Moisture Contents. It is expected that the physical properties of a polymer are intimately related to the volume occupied by the microvoids in it. In order to infer free volume in various test samples, it was decided to measure their saturation moisture contents since the latter are directly related to the accessible free volume. The procedure for measuring the saturation moisture contents of the test samples was as follows: The samples were first saturated with water by immersing them in distilled water at 90°C for several days until their weights became constant. They were then desiccated in a vacuum oven at 100°C for several days until there was no further reduction in their weights. The saturation moisture contents were then determined by comparing the corresponding saturated and desiccated weights for each sample. The results are summarized in Table II.

TABLE II. Summary of Saturation Moisture Contents of the Test Samples With Various Additives

No.	Specimen	Saturation Moisture Content ^(*)
1	BDSDA/ODA/MPD 422 Copolyimide (REF)	1.52 _± 0.01 %
2	422 + 5% BDSDA/AN	1.45 _± 0.03 %
3	422 + 5% ODA/PA	1.41 _± 0.01 %
4	422 + 5% MPD/PA	1.36 _± 0.02 %
5	422 + 10% BDSDA/AN	1.27 _± 0.02 %

(*) These values represent average of saturation moisture contents of two samples of each material prepared under identical conditions.

(d) Measurement of Positron Annihilation Characteristics. Positron lifetime spectra were measured using a standard fast-slow coincidence system⁽⁴⁾. The resolution of the system, as measured with a Co⁶⁰ gamma ray source, was approximately 400 picoseconds. The test samples were fabricated in the form of 1" dia x 0.1" thick discs. A 10 µc Na²² source was sandwiched between the two sample discs and the entire source-sample assembly was placed between two scintillation detectors. Figure 2 shows a schematic diagram of the experimental system.

Detailed lifetime measurements were made in the reference targets and the targets containing short-chain additives. The largest impact on positron annihilation characteristics was noted for the samples containing 10 percent BDSDA/AN. Typical lifetime spectra required about 24 hours to obtain the statistics necessary for accurate deconvolution. The spectra were analyzed for constituent lifetime components using the RESOLUTION computer program⁽⁵⁾ which automatically calculated the lifetimes and relative intensities of various components after subtracting a flat background from the raw spectrum. Instead of trying to decide how many lifetime components were present in each spectrum, all the spectra were fitted with only two components since such analyses are expected⁽⁶⁾ to reflect the main changes in the annihilation characteristics with the changing test sample molecular structure. The positron lifetime results are summarized in Table III.

TABLE III. Summary of Positron Lifetime Characteristics in the Test Samples

No.	Specimen	Positron Lifetime Characteristics ^(*)		
		τ_1 (ps)	τ_2 (ps)	I_2 (%)
1	(BDSDA/ODA/MPD [422] Copolyimide (REFERENCE))	379 \pm 2	1715 \pm 60	4.9 \pm 0.5
2	([422] + 10% BDSDA/AN Additive Copolyimide)	382 \pm 2	1604 \pm 60	5.7 \pm 0.5

(*) Only lifetime characteristics in copolyimide sample containing 10% BDSDA/AN are shown here. The data in other samples containing lower concentrations of short-chain additives were correspondingly less impacted.

DISCUSSION

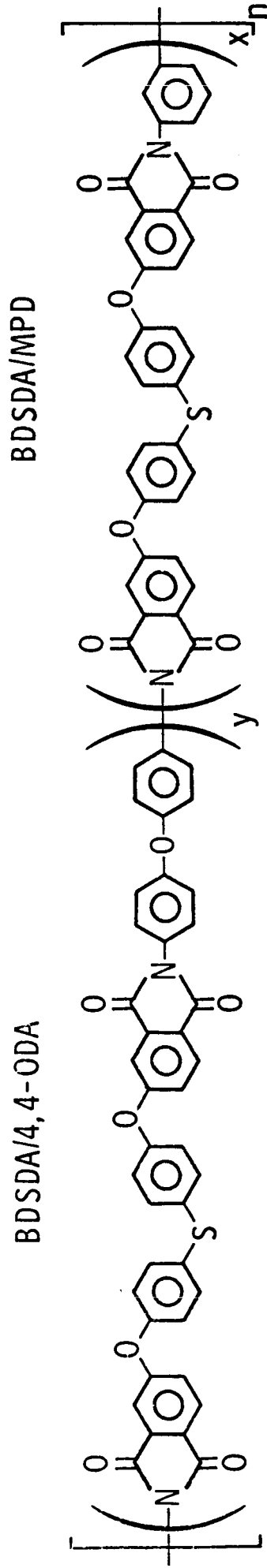
An examination of the saturation moisture contents summarized in Table II shows that the free volume in the [422] copolyimide decrease systemetrically as we add 5% BDSDA/AN, ODA/PA, and MPD/PA, respectively. It thus appears that MPD/PA is the most effective short-chain additive for making the [422] copolyimide more compact, and consequently, denser. But doubling the concentration of BDSDA/AN appears to have a disproportionately large effect on free volume in the base polymer. The positron annihilation data in the modified specimen, summarized in Table III, is also consistent with this large reduction in free volume. A concomitant increase in the long lifetime component intensity suggests that most of the free electrons have been engaged in strengthening the electronic bonds between various segments of the molecular chains.

CONCLUDING REMARKS

The effects of several short-chain processing additives on the physical properties of the BDSDA/ODA/MPD [422] copolyimide have been investigated. It appears that a 10 percent addition of BDSDA/AN produces the most desirable effect of strengthening the copolyimide chain interactions and making it environmentally stable. It ostensibly does so by increasing the chain packing density and reducing the free volume in the host material.

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For 413 copolyimide, $y = 1$, $x = 3$

For 422 copolyimide, $y = 2$, $x = 2$ (50-50 copolymer)

For 431 copolyimide, $y = 3$, $x = 1$

Figure 1. - Molecular structure of the BDSDA/ODA/MPD copolyimide.

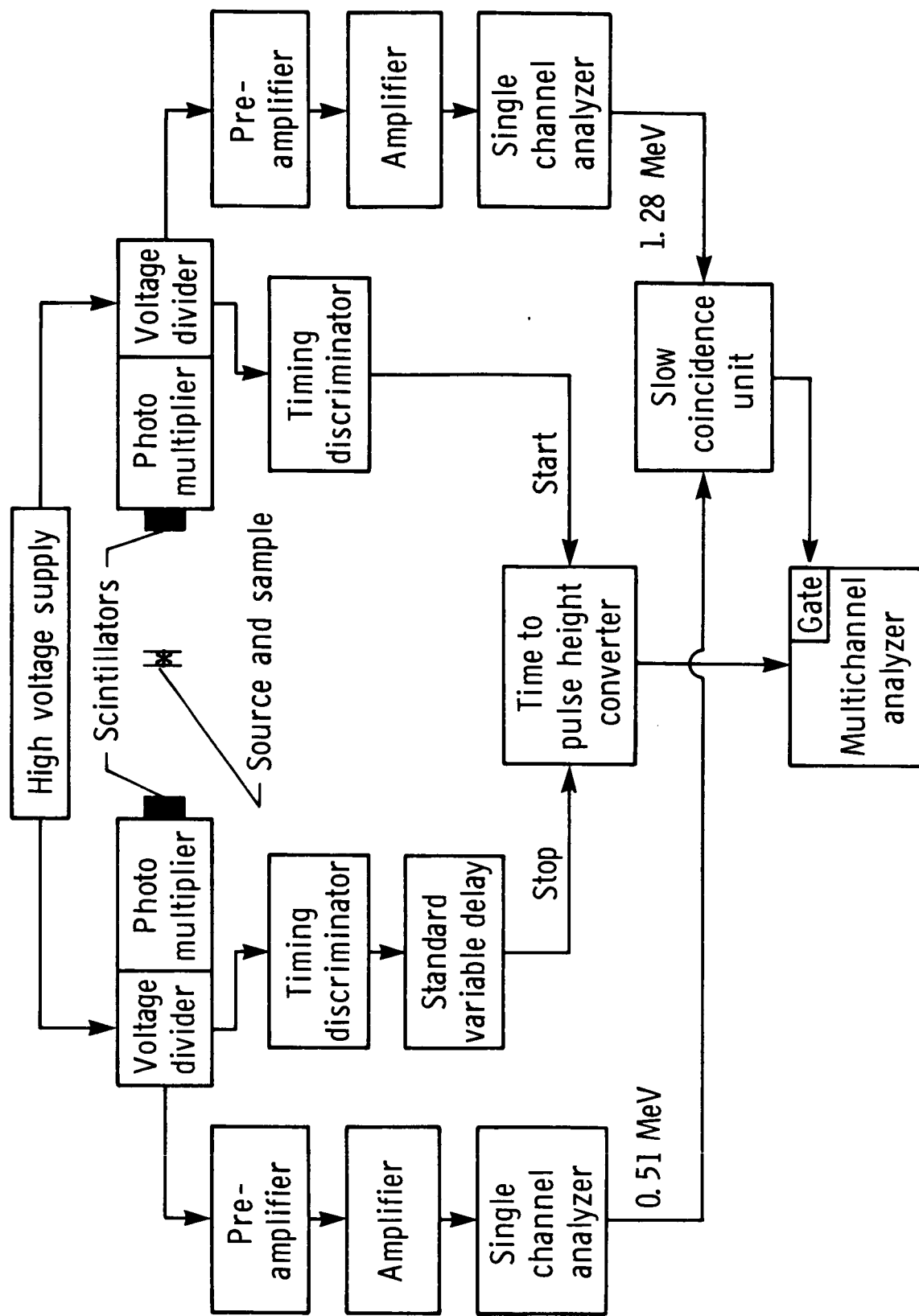


Figure 2 - Fast-slow coincidence system for determining positron lifetime spectra.

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