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ADDITION POLYIMIDE END CAP STUDY

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INTRODUCTION

Addition polyimides have evolved as a compromise between the need for a thermally stable polymer system and the need to be able to process a material into a usable form. The linear aromatic polymer systems that were initially developed were virtually impossible to process once they had attained a high molecular weight. Since these polymers had such exceptional thermal properties, efforts were made to overcome this shortcoming by capping short chains (oligomers) of the polyimide with end groups that had latent reactivity.

The first example of imides of this type was the norbornene end-capped P-13N system which was developed by TRW, Incorporated (ref. 1-2). For this addition-type polyimide a prepolymer of 1300 molecular weight was prepared with a norbornene cap on each end of the chain. This system had enough flow to be consolidated into an essentially void-free molding. After the total conversion in the 150-220°C range of the amide acid to the imide, set-up of the P-13N was effected through the norbornene end caps in the 220-320°C cure range.

The problem with this norbornene-capped system is two-fold. First, the norbornene is an aliphatic system which detracts from the thermal stability of the resulting polymer. Second, the norbornene system must be cured under pressure or it undergoes a retrograde Diels-Alder reaction to yield a volatile component, cyclopentadiene (ref. 3), which is detrimental in the preparation of low-void parts. Together, these problems with norbornene-capped, oligomer, aromatic imides have prompted research into alternate end caps for addition polyimides.

N81-14081#

PROGRAM OUTLINE

The primary objective of this research program was to screen and characterize addition polyimides with various end caps for adhesive applications for 120-250°C use. Another objective was to find a crosslinking system which would cure without the evolution of volatiles because these adhesive applications include the large-area bonding of metals and composites. Volatiles will cause unacceptable blistering in the bonded area.

The approach taken for this research effort was to choose a known adhesive system based on the conventional norbornene-capped oligomer, LARC-13 (Ref. 6) for comparison. This material has been shown to perform well at ambient and elevated temperature conditions as an adhesive. All of the novel oligomeric systems in this investigation are compared to LARC-13.

The differential scanning calorimetry (DSC) data were generated using the oligomers in their powdered forms. The adhesive data were from simple lap shear specimens bonded with the adhesive on a glass carrier cloth.

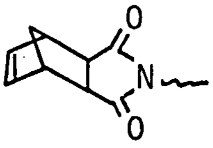
OBJECTIVE: TO SCREEN AND CHARACTERIZE ADDITION POLYIMIDES MADE WITH REACTIVE END GROUPS WHICH ALLOW A LOW-VOLATILE CURE FOR ADHESIVE APPLICATIONS.

APPROACH: A SYSTEMATIC VARIATION IN THE STRUCTURE OF REACTIVE END GROUPS IN A KNOWN ADDITION POLYIMIDE ADHESIVE.

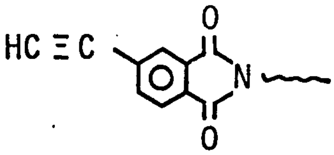
APPLICATION: STRUCTURAL ADHESIVE

END GROUPS

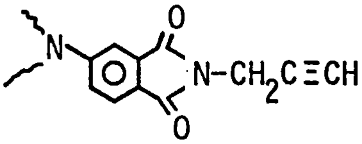
The end groups investigated in this study are shown in the table below. The state-of-the-art addition polyimides are primarily based on norbornene capped systems which are prepared from commercially available 5-norbornene-2,3-dicarboxylic anhydride (ref. 1,2,4,5 & 6). The acetylene capped system was prepared from the corresponding anhydride which was recently prepared by Gulf R&D, Pittsburg, PA, and characterized for addition polyimide use by Hergenrother (ref. 7). The N-propargyl imide capped system was prepared using 4-amino-N-propargylphthalimide. This novel compound was prepared by Pratt at Mississippi University for Women on a research grant from NASA Langley Research Center (ref. 8). The cyclohexene and maleic end groups were derived from commercially available cis-4-cyclohexene-1,2-dicarboxylic anhydride and maleic anhydride, respectively.



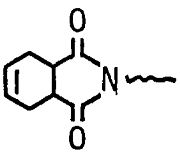
NORBORNENE



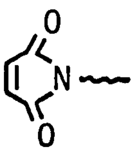
PHENYLACETYLENE



N-PROPARGYL



CYCLOHEXENE

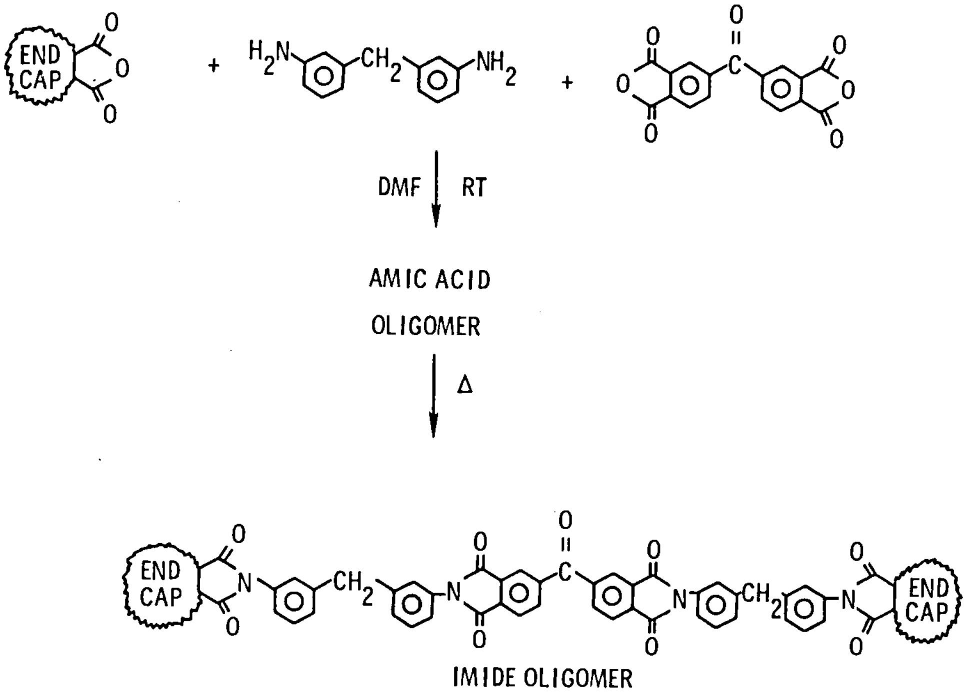


MALEIC

OLIGOMER PREPARATION

Anhydride Caps

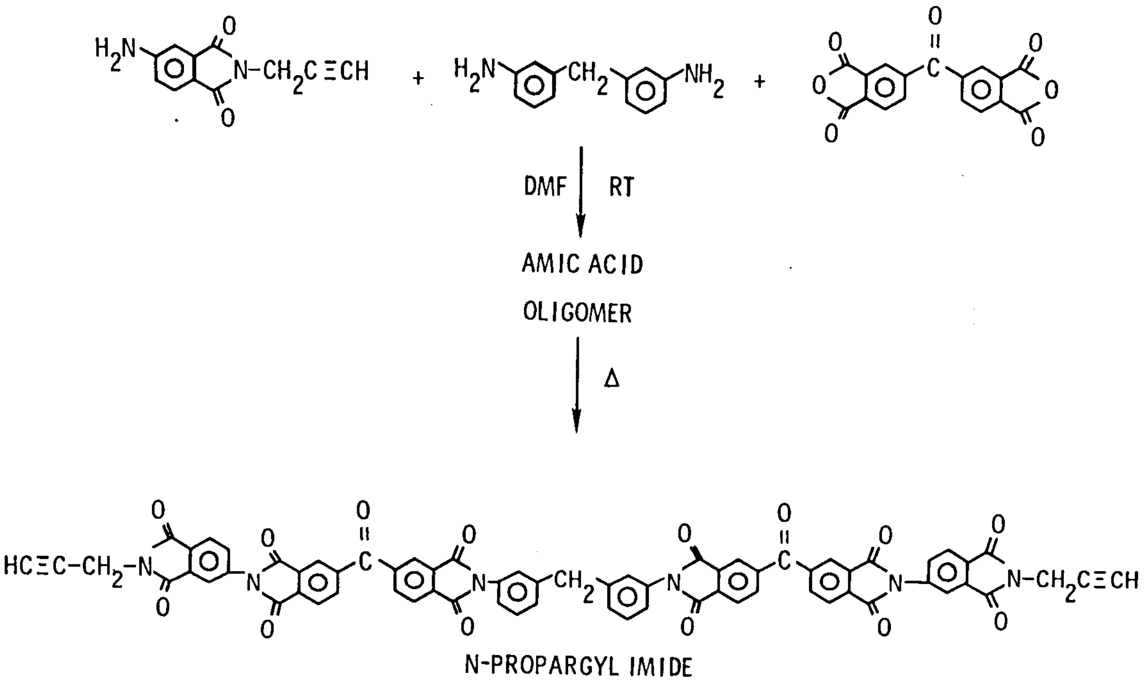
The oligomer preparation for the three anhydride-capped systems (norbornene, phenylacetylene and cyclohexene) followed the route outlined in the scheme below. The preparation of the amic acid was effected by dissolving the 3,3'-methylenedianiline (3,3'MDA) in N,N-dimethylformamide (DMF) at ambient temperature. The two anhydrides were added as solids in ten equal portions over an eight-hour period. This slow addition procedure was used to ensure proper chain extension with the difunctional benzophenone tetracarboxylic acid dianhydride (BTDA). This procedure was necessitated because of the apparent higher degree of reactivity of the end-capped anhydrides over BTDA (this may be due to a higher degree of solubility). After the last addition of the anhydrides the reaction mixture was allowed to stir overnight. The amic acid oligomers were converted to the corresponding imide by heating to 150-180°C after removal of the solvent.



OLIGOMER PREPARATION

N-Propargyl Cap

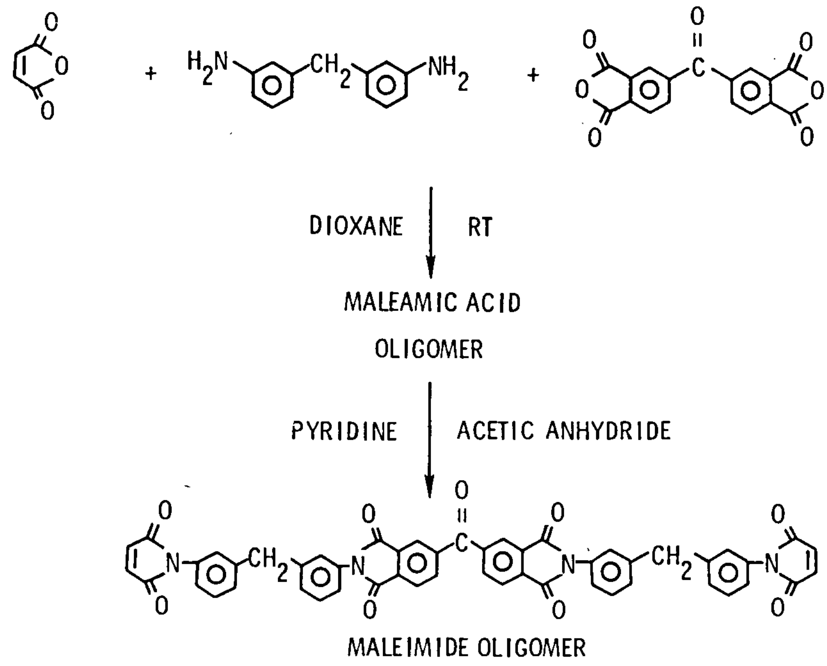
This oligomer preparation was slightly different from the anhydride-capped systems because in this case the end cap is reacted on through an amine function on the 3-amino-N-propargylphthalimide. In all of the other oligomer preparations the end group was reacted onto the system through an anhydride function. This mechanism for attachment results in a larger number of imide groups per oligomer for the N-propargyl-capped system. The reaction mixture after stirring overnight was converted to the imide by the normal thermal treatment.



OLIGOMER PREPARATION

Maleimide Cap

The preparation of the maleic end-capped oligomer was accomplished in a slightly different manner than for the other anhydride-capped systems. This difference was necessitated because thermal treatment of the maleamic acid oligomer leads to partial isomerism by the end group to the fumaric structure which cannot result in a thermally stable imide. In order to accomplish conversion to the imide without isomerism, the amic acid was isolated by precipitation into water followed by filtration and drying. Dehydration to the imide was accomplished using acetic anhydride as the dehydration agent in pyridine. Subsequent isolation of the maleimide was effected by precipitation into water, filtration and washing the filtrate with copious amounts of water to eliminate traces of acetic acid (the by-product of the dehydration).



MELT-FLOW PROPERTIES

The melt-flow temperatures as characterized in the table are those determined from differential scanning calorimetry (DSC). This softening or melting is characterized by an endotherm on DSC charts. The broadness of some of the melt-flow ranges may be due to a distribution of molecular weight species for each system. This distribution for the norbornene-capped system has been shown to be due to the double end capping of the methylenedianiline by the norbornene anhydride (Ref. 9). This appears to be a thermodynamic or kinetic anomaly for this system.

The base norbornene system begins to soften around 160°C and remains soft until the crosslinking sets up the polymer. The acetylene, propargyl and cyclohexene end-capped materials all began to melt about 20-30°C lower than the norbornene system. This lower-melting property is a distinct advantage in that it allows for hot-melt impregnation of adhesive cloths if a sufficient spread exists between the melt endotherm temperature and the temperature associated with the crosslinking or cure. The melt flow temperature for the maleic capped oligomer was substantially higher than for the norbornene-capped oligomer.

OLIGOMER SYSTEM	MELT-FLOW TEMPERATURE, °C
NORBORNENE	160 - 250
ACETYLENE	140 - 160
N-PROPARGYL	130 - 160
CYCLOHEXENE	140 - 185
MALEIC	185 - 212

CURE EXOTHERMS

The cure exotherm as obtained by differential scanning calorimetry (DSC) is the temperature region where the functional end groups react. In the table below this region is characterized for each oligomer system by the onset temperature and the temperature where the exotherm maximized. The difference between the onset and maximum temperatures is an indication of how rapid the cure is for each system. The cure exotherm onset for a usable system should be separated from the melt endotherm by several degrees in order to allow for melt impregnation of adhesive cloths without curing the system. The exotherms for the norbornene, N-propargyl and cyclohexene are sufficiently separated; the acetylene and maleic are borderline. The maximum exotherm for the cyclohexene system is high at 415°C which indicates that a relatively slow cure is occurring since the onset exotherm is near those of the norbornene and N-propargyl systems.

OLIGOMER SYSTEM	CURE EXOTHERM, °C	
	ONSET	MAXIMUM
NORBORNENE	275	357
ACETYLENE	175	250
N-PROPARGYL	250	330
CYCLOHEXENE	280	415
MALEIC	240	317

GLASS TRANSITION TEMPERATURE

The apparent glass transition temperature (Tg) for each cured system was determined by thermomechanical analysis (TMA) using the samples from the DSC which had been heated at 10°C/minute from ambient to 400°C and allowed to cool. These samples were characterized for softening by using the DuPont 943 Thermomechanical Analyzer interfaced to the DuPont 990 Thermal Analyzer base unit. A hemispherical-tipped quartz probe under a 15 gram load was used for penetration of the sample.

The Tg for the norbornene, acetylene and N-propargyl systems were quite close, indicating similar crosslink densities. The softening temperature for the maleimide was slightly lower, and the cyclohexene polymer had a considerably lower Tg. These low Tg's were probably due to a slower reaction rate during the cure of these systems. The Tg's would likely have increased if these two systems had been allowed to cure for a longer time at elevated temperature.

OLIGOMER SYSTEM	GLASS TRANSITION TEMP., °C *
NORBORNENE	248
ACETYLENE	248
N-PROPARGYL	235
CYCLOHEXENE	189
MALEIC	220

* ALL SYSTEMS CURED TO 400° C AND T_g DETERMINED BY THERMOMECHANICAL ANALYSES

THERMAL STABILITY

The thermal stabilities for the cured systems were determined by using the DSC-cured polymers and subjecting them to a 2-1/2°C per minute temperature increase in static air. This procedure was carried out using a Perkin-Elmer UU-1 Temperature Program Control, AR-2 Autobalance and TGS-2 Thermogravimetric System. The thermal stabilities were similar for all of the systems except the maleimide which lost fifty percent of its weight at 60-75°C lower than the others. These dynamic thermogravimetric analyses for highly crosslinked systems are only an indication of short-term performance capabilities of polymers. More relevant data on longer-term stabilities were obtained from actual thermal aging at 232°C.

OLIGOMER SYSTEM	TEMP. FOR 50 % WEIGHT LOSS, °C *
NORBORNENE	575
ACETYLENE	560
N-PROPARGYL	560
CYCLOHEXENE	575
MALEIC	500

*SAMPLES HEATED AT 2 - 1/2°C/MIN IN STATIC AIR

ADHESIVE PROPERTIES

Adhesive cloths of each system were prepared by coating the oligomeric amic acid onto a woven glass carrier cloth (style 112E-glass) coated with an aminosilane coupling agent and driving off the solvent. Adhesive cloth thickness was generally built up to 0.03 cm (12 mils) with repeated coatings. After the desired thickness was obtained the cloth was subjected to temperatures of 100°, 200° and 225°C for one hour each to further drive off solvent and to convert the amic acid to the imide.

The adhesive data in the table were obtained by testing bonded lap shear samples (ASTM D-1002) prepared with titanium 6-4 adherends[a]. The bonding cycle of - RT → 300°C at 5°C/minute; apply 345 Pa (50 psi) after 30 minutes; hold 30 minutes - was used for each adhesive. All adhesives had adequate flow during the bonding operation. The adhesive test data for the first three systems (norbornene, acetylene and N-propargyl) were exceptionally good at both room temperature and 232°C. The cyclohexene and maleic capped adhesives formed poor bonds and were not carried into the aging program.

OLIGOMER SYSTEM	LAP SHEAR STRENGTH,* psi (MPa)	
	INITIAL	
	RT	232°C
NORBORNENE	3200 (22.1)	2600 (17.9)
ACETYLENE	2900 (20.0)	2500 (17.2)
N-PROPARGYL	3100 (21.4)	2800 (19.3)
CYCLOHEXENE	BROKE CUTTING	BROKE CUTTING
MALEIC	1000 (6.9)	FAILED ON HEAT UP

* TITANIUM ADHERENDS

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[a] Each data point represents the average of four samples variability was ± 10%

ADHESIVE AGING PROPERTIES

The three polymer systems that made good adhesives were subject to an aging study to determine their relative stabilities. The norbornene or LARC-13 system had already been shown to have excellent adhesive properties (Ref. 6) and data on this system are in the following table. The LARC-13 data show a drop after aging for 1000 hours in air at 232°C. A slight drop is expected for these thermoset systems at room temperature due to further crosslinking, but the fall off at the 232°C test temperature is indicative of polymer degradation. The adhesive properties for the N-propargyl system were quite poor after 1000 hours at 232°C, but the acetylene system was forty percent higher at 232°C after aging than the base LARC-13.

Since the propargyl system did not perform well at 232°C and it exhibited excellent initial strengths, aging was conducted at 121°C. After 1000 hours at this temperature, this adhesive performed well when tested at room temperature and 121°C. This data places the stability of these capped systems in the order acetylene > norbornene > propargyl.

LAP SHEAR STRENGTH, psi (MPa)

ADHESIVE	INITIAL			AFTER 1000 hrs @ 121° C		AFTER 1000 hrs @ 232° C	
	RT	121° C	232° C	RT	121° C	RT	232° C
LARC-13	3200 (22.1)	-	2600 (17.9)	-	-	2600 (17.9)	1960 (13.5)
ACETYLENE	2900 (20.0)	-	2500 (17.2)	-	-	2500 (17.2)	2800 (19.3)
PROPARGYL	3100 (21.4)	2700 (18.6)	2800 (19.3)	2400 (16.5)	2200 (15.2)	800 (5.5)	1000 (6.9)

SUMMARY

Four novel end-capped oligomeric imides were prepared and characterized for melt-flow, cure exotherm, thermal stability, glass transition temperature, and adhesive properties. These systems were capped with the following thermally reactive groups: acetylene, propargyl, cyclohexene and maleic. These functionally end-capped oligomers were compared to the known norbornene capped LARC-13. The four systems exhibited varied properties in their melt-flow temperatures and cure exotherms. The cyclohexene-capped material exhibited a slow cure as evidenced by its cure exotherm and its low glass transition temperature. The maleic-capped material proved to have the poorest thermal stability. Two systems, acetylene and propargyl, exhibited initial adhesive properties equal to LARC-13. Subsequent thermal aging at 232°C proved the acetylene system to have better, and the propargyl system worse retention of adhesive lap shear strength than LARC-13. However, the propargyl adhesive exhibited good strength retention when the aging temperature was lowered to 121°C.

REFERENCES

1. Lubowitz, H. R.: U.S. Patent 3,528,950, Sept. 15, 1970.
2. Lubowitz, H. R.; Jones, J. F.; Vaughan, R. W.; and Burns, E. A.: SAMPE Symposium Proceedings, 15, 1971, p. 59.
3. Ogliaruso, M. A.; Romanelli, M. G.; and Becker, E. I.: Chem. Reviews, 65, 1971, p. 261.
4. Serafini, T. T.; Delvigs, P.; and Lightsey, G. R.: J. Applied Polym. Sci., 16(4), 1972, p. 905.
5. St. Clair, T. L. and Jewell, R. A.: SAMPE Tech. Conf. Proceedings, 8, 1976, p. 82.
6. St. Clair, T. L. and Progar, D. J.: SAMPE Symposium Proceedings, 24, 1979, p. 1081.
7. Hergenrother, P.M.: Polymer Preprints, 21(1), 1980, p. 81.
8. Pratt, J. R.: NASA CR-159378, 1979.
9. Young, P. R. and Sykes, G. F.: Org. Plastics and Coatings, 40(1), 1979, p. 935.

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16. Abstract

Oligomeric polyimides were prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-methylenedianiline which were end-capped with functionally reactive moities which cause crosslinking when the oligomers are heated to 200-400°C. The syntheses of the oligomers are outlined. The thermolysis of the oligomers was studied by differential scanning calorimetry and the resulting polymers were characterized by differential thermal analysis and adhesive performance. The adhesive data include lap shear strengths on titanium 6-4 adherends both before and after aging for 1000 hours at 121°C and/or 232°C.

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