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SOLID STATE INTERCHAIN TRANSESTERIFICATION REACTIONS IN MACROMOLECULES

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Abstract: Interchain transesterification reactions (ITR) play an important role in high temperature synthesis of most linear polyesters. For example, polyethylene terephthalate (PET) is prepared commercially by heating and distillation of ethylene glycol from a glycol capped oligomer of PET. In this paper, the potential importance of ITR to effect a much wider range of reactions and process is examined. For example, the ability to control the sequence distribution in linear copolyesters is described. In particular, it is shown that one can induce a random sequence distribution in copolyesters by ITR or, conversely, develop an ordered sequence from a random copolyester again by ITR. In one family of liquid crystalline copolyesters an unusual competition between ordering and a thermal Fries rearrangement is described. A whole new family of crosslinked copolyesters has been developed based on this knowledge of ITR. Solid state processing of cured copolyesters into finished articles by ITR has also been demonstrated. These crosslinked copolyesters can be depolymerized back to the starting oligomers by a reverse ITR, providing for the first time a recyclable thermosetting resin.

CONTROL OF SEQUENCE DISTRIBUTION IN COPOLYESTERS

Polyesters can undergo several types of high temperature reactions via ITR: further polymerization, randomization, and sequence ordering. Degradation reactions may also occur and one example is presented at the end of this section.

Randomization

In the past, there has been considerable debate over the nature of the sequence distribution in liquid crystalline copolyesters which have been heated in the temperature range where the polymer is nematic. Some workers have argued that these systems are stable in the

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melt,[1] others claim that they undergo ordering,[2] while we have argued that the dominant process is randomization through ITR.[3]

The potential for very rapid randomizing processes in the copolyesters has been conclusively demonstrated by heating a 50/50 mixture of the two homopolymers of PHBA and PHNA at 450°C at a pressure of only several hundred psi.[3] A relatively low viscosity melt was formed which extruded from the cracks in the mold within a few seconds. DSC measurements of this new material indicated a crystal-nematic transition temperature (T_{cn}) of ~260°C which is consistent with a 50/50 random copolymer (see Figure 1). Benzoic-naphthoic and naphthoic-benzoic diad sequences could be easily detected from the ^{13}C NMR spectrum of the extrudate shown in Figure 2a. Comparison of this ^{13}C NMR with the random PHBA/HNA copolymer (see Figure 2a and 2b) indicates that the structures are identical. It is estimated that ITR reactions at this elevated temperature occur at rates in excess of 100 ester interchange reactions/chain/second.[3]

The ability of the ester groups to undergo rapid ITR suggests the potential use of the LCP coatings as high temperature adhesives. In fact, the lap shear strength of 73/27 HBA/HNA coated on aluminum shown in Figure 3 indicates reasonable adhesive properties.[4]

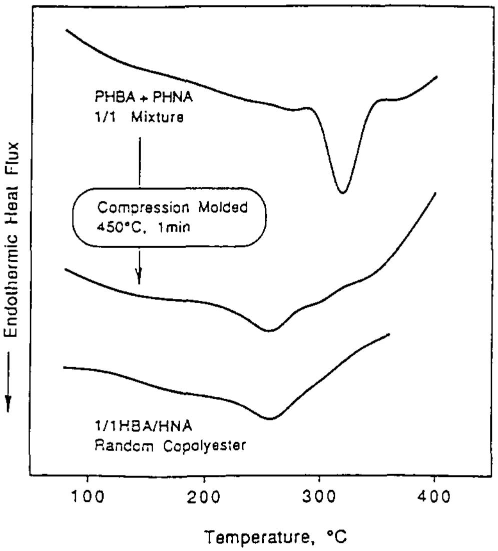

Figure 1. DSC of PHBA and PHNA mixture, compression molded mixture, and a 1/1 PHBA/HNA random copolyester.

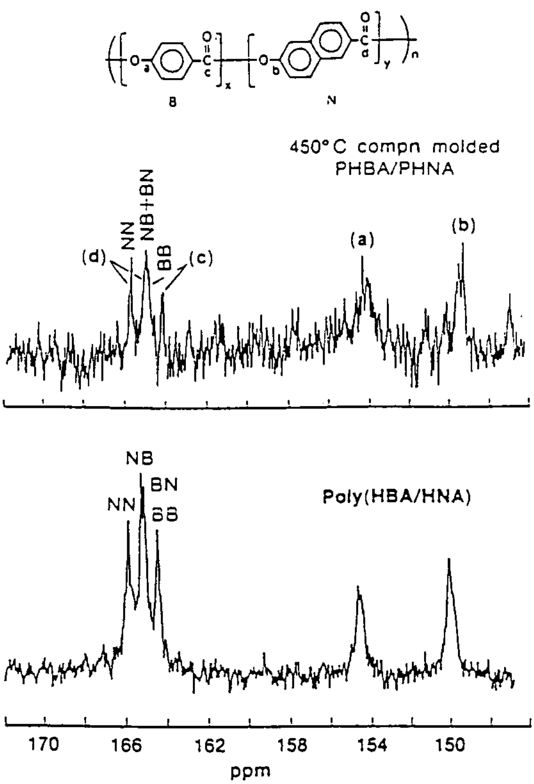

Figure 2. Comparison of ^{13}C NMR spectra of the compression molded mixture of PHBA and PHNA with that of random PHBA/HNA copolymer.

In all cases, the failure is cohesive and never adhesive which implies that the nematic melt is able to orient at the polymer–metal interface on cooling from the melt to minimize the mismatch in coefficient of thermal expansion (CTE). Presumably, while cooling from the melt, the LCP organizes at the interface to minimize the stress associated with contraction of the substrate and thus approximate the CTE of the substrate. This process should continue down to the T_g of the nematic melt.

It is noteworthy that these LCP coatings provide excellent protection for metal substrates against acids, moisture, abrasion, and wear.[5] On the other hand, these coatings possess several limitations. The LCP's must be coated as a high viscosity melt at temperatures greater than 300°C onto the metal substrate. The strength at high temperatures of the HBA/HNA is limited to 130-150°C due to the relatively low degree of crystallinity.[6] The anisotropic nature of the LCP also appears to provide a limit to the lap shear strength of 1/2 to 2/3 the values observed with epoxies. This should be expected since the transverse mechanical properties of highly anisotropic films are low due to the tendency of these rod-like chains to preferentially orient with reduced bonding in the perpendicular direction.

Sequence Ordering

A very unusual process occurs upon annealing the copolyesters near their T_{cn}, namely, a dramatic increase in transition temperature by 40°C-75°C.[7-9] As would be expected, annealing at well below the T_{cn} leads to a significant increase in transition enthalpy with little change in the melting temperature. Diffusion processes dominate under these conditions and it is well accepted that increased crystallinity occurs by a physical process.[7-11] ^{13}C NMR analyses of 50/50 HBA/HNA[3] and 73/27 HBA/HNA[12] copolyesters annealed well below the T_{cn} do not indicate any change in diad sequence distribution.

On the other hand, annealing the copolyesters near their T_{cn} not only changes the nature of the transition from crystal to nematic to crystal to smectic[13], but is accompanied by a change in crystal structure (hexagonal to orthorhombic)[8], increase in density,[14] and a sharp decrease in solubility. The increase in the transition temperature has been demonstrated throughout the entire HBA/HNA compositional range (Figure 4).[15,16]

Several sharply different interpretations have been proposed to explain the mechanism by which this process occurs. Winter proposes that ordering is due to a physical process which involves the melting of crystallites when annealing near T_{cn}.[7] Melting is followed by nucleation and crystallization of longer ordered sequences already present within the random copolyester. From a simple statistical analysis, we have estimated that the probability for pre-existing long sequences of ordered units within a two-dimensional array is less than 1%.[15,16] Hence, this proposal can be ruled out since the long ordered sequences necessary for nucleation and growth of higher melting crystals do not exist in a random copolyester.

Yoon has argued that the increase in melting during annealing near the T_{cn} is a result of molecular weight increases because of the long annealing times.[17] However, a recent report by Windle shows that when the molecular weight of a 75/25 HBA/HNA copolyester is increased from 8,600 g/mol to 30,000 g/mol the increase in melting point is only 12 °C (from 283°C to 295°C).[18] Hence, it is unrealistic to attribute changes of up to 75°C to an increase in molecular weight.

Geil has suggested that an increase in crystal size and perfection via a physical process is occurring.[19] Contrary experimental evidence includes results which show there is no difference in the DSC traces of annealed samples slow cooled (1°C/min) from the annealing temperature versus quenched.[15] One would expect crystalline domains with increased size and perfection formed from a physical process would be sensitive to heating conditions, thus slow cooling would result in a larger endotherm.

The ordering mechanism that we propose is chemical in nature and depends on ITR reactions within the existing crystallites present in the copolyester. Thus, near T_{cn} the end groups have sufficient mobility within the crystallites to facilitate ordering of the microstructure

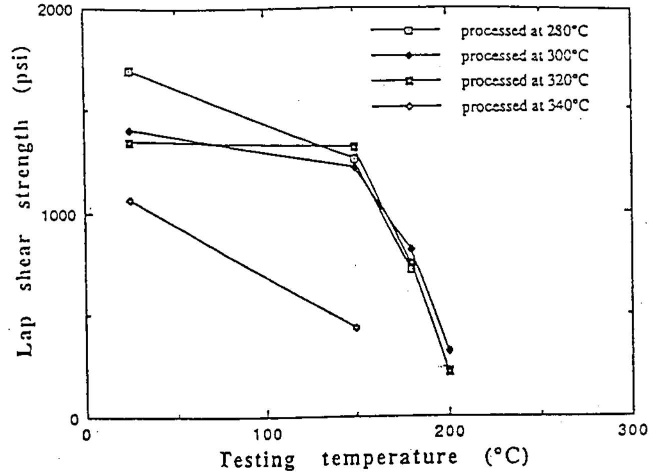

Figure 3. Effect of the processing temperature on the lap shear strength of 73/27 HBA/HNA bonded to aluminum for specimens tested at different temperatures.

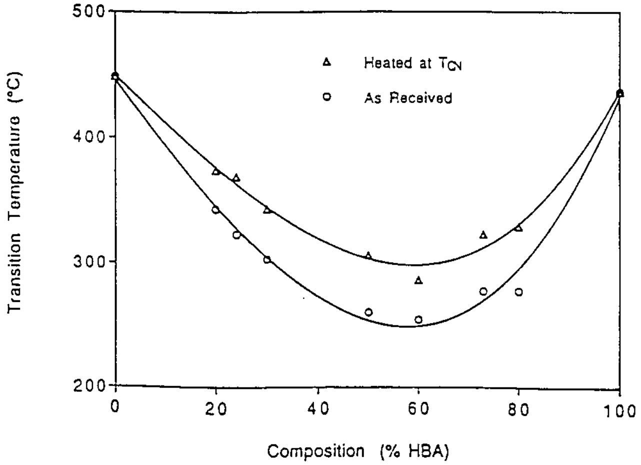

Figure 4. Transition temperatures as a function of composition of HBA/HNA copolyesters.

through ITR. These reactions can only occur in the crystallites, since in the coexisting nematic melt no templates are present to promote ordering.[3] The driving force for chemical ordering reactions arise from the improved packing and correspondingly higher density associated with a more ordered structure. ITR allows for improved ordering of sequences, but not necessarily complete ordering, since mobility within the crystallites should drop significantly as the transition temperature begins to increase.

Using ^{13}C NMR, one can follow the sequence ordering of HBA/HNA (5000 g/mol) containing a HBA ^{13}C carbonyl carbon as the concentration of diad sequences changes during anneal.[20] ^{13}C NMR of samples annealed at 190°C for 24 and 48 hours (to build crystallinity) revealed no changes in the benzoic-naphthoic (BN) and benzoic-benzoic (BB) diad ratios. However, the ratio of BN to BB does change upon annealing near the T_{cn}. Upon annealing near the T_{cn} for 24 hours, there is a 1.7% increase in BN diads of the entire sample. Since these changes are occurring in the crystalline regions only (~15%), this represents a change of ~11%. Increasing the anneal time from 24 to 48 hours further increases the ordering from random to alternating (2.1% increase in BN diads). This provides reasonably conclusive evidence that ITR occurs leading to sequence ordering.

Presumably, one should be able to increase the degree of order by further raising the annealing temperature. This has in fact been demonstrated with the Xydar family of liquid crystalline copolyesters. Thus, the DSC results in Figure 5 reveal that Xydar SRT900 (HBA/BP/TA/Isophthalic acid: 2/1/0.6/0.4) initially randomized at 400°C for 15 minutes and annealed at 230°C for 10 hours has a T_{cn} of 290°C. Annealing at 280°C for 5 hours increases the T_{cn} to 350°C and then an additional anneal at 330°C for 10 hours increases the T_{cn} to 399°C. Attempts to carry out the same kind of process with the PHBA/HNA has led to a surprising degradation reaction which is discussed in the next paragraph.

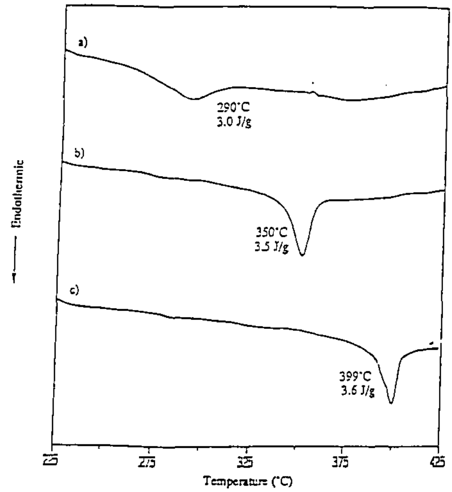

Figure 5. Xydar SRT900 (a) randomized at 400°C for 15 minutes, annealed at 230°C for 10 hours, (b) (a) annealed at 280°C for 5 hours, and (c) (b) annealed at 330°C for 10 hours.

Attempts to stepwise anneal the HBA/HNA 73/27, 50/50, and 24/76 compositions resulted in each case an insoluble, non-crystalline, non melting resin.[16] Using FT-IR, some insights into the degradation process have been obtained. FT-IR of 73/27 HBA/HNA biaxially oriented film obtained from Foster-Miller and step-annealed at 200°C for 64 hours, 240°C for 24 hours, 270°C for 24 hours, and 300°C for 5 hours are shown in Figure 6. The as-received HBA/HNA has a hydroxy stretch at 3454 cm^{-1} and ester carbonyl stretch at 1754 cm^{-1}. Upon ordering and further annealing, the structure changes significantly. The hydroxy relative peak height increases while the carbonyl stretch decreases indicative of a Fries rearrangement. Presumably, an interchain Fries rearrangement would cause crosslinking which would result in the insoluble, non melting resin. Also, the presence of the hydoxy stretch in the as-received film suggests some prior degradation of the film during extrusion at 290°C in air.

CROSSLINKABLE AROMATIC POLYESTERS

As mentioned earlier, there are several drawbacks affecting LCP usage including cost, processability, and their anisotropic nature. We have recently reported the successful design of a new family of crosslinked aromatic copolyesters with outstanding high temperature

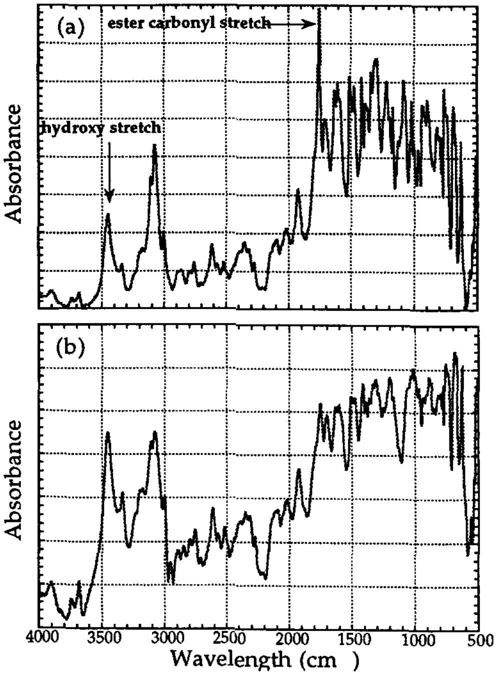

Figure 6. FT-IR analysis of 73/27 HBA/HNA (a) as-received and (b) step annealed 200°C for 64 hours, 240°C for 24 hours, 270°C for 24 hours, and 300°C for 5 hours.

properties.[21] The precursor oligomer is made up of a two component system where one oligomer has acetoxy end groups and the other oligomer has carboxylic acid end groups. The mixture of the two oligomers melts at 100-220°C, depending on oligomer molecular weight and composition. The melting temperature is well below the cure temperature which begins at 240°C and is completed near 300°C. One can design systems which have relatively low viscosities by selecting the appropriate monomer feed ratio and molecular weight, thus eliminating the need for solvents. In certain cases, liquid crystalline character can be observed in the oligomeric melts due to the presence of longer rod-like units between branching sites. Interestingly, the optical birefringence persists during curing, suggesting the presence of local order in the crosslinked structure.[22]

In Table 1, some of the novel properties of these polymers are described. The outstanding feature of this new thermoset family compared to epoxies and phenolics is its excellent high temperature stability. The DMA scan in Figure 7 shows nearly 100% retention of flexural storage modulus (E') at 200°C and 60% at 350°C. The DMA scan also shows that the molecular weight between crosslinks can be tailored to improve the retention in mechanicals at elevated temperatures. TGA of the aromatic copolyester resin shows a short term thermal stability to 450°C in nitrogen.

One unique feature of these thermosets is the ability to use ITR to recycle the crosslinked polyester resins.[23] The process depends on an acetolysis of the crosslinked polyester network leading to multifunctional oligomers with acetoxy and carboxylic acid end groups. These oligomers can react again upon heating to give the identical crosslinked copolyester system.

Another unique feature of these resins is the ability to foam the structure using the acetic acid by-product of the crosslinking reaction. Foaming provides a pathway to lower the dielectric constant of the thermoset enabling the material to be used as a substrate in electronic packaging. The crosslinked aromatic polyester can also be used as a structural foam. The foam, when heated at 300°C for 12 hours, shows little dimension change as measured by a thermal mechanical analyzer equipped with a penetration probe loaded at 50 psi.

Adhesive Bond Formation

Considerable effort has been made to improve the lap shear strength of the adhesive bond formed by solid state ITR at the interface between the crosslinked aromatic copolyesters. Typically, the lap shear strength averages about 1900 psi with failure always at the polymer–metal interface.[24] A matrix of experiments was designed to determine if bonding at the polymer–metal interface could be improved. These included the use of milled glass fiber reinforcement, a specially designed liquid crystalline copolyester thermoset, different metal substrates such as titanium, and various substrate surface pretreatments. A most dramatic increase in bond strength of 50% was achieved by reducing the bondline thickness from 350 μm to 100 μm.[25] The failure mode was still adhesive, so the likelihood to obtain even higher lap shear strengths exist with improved surface treatment. However, the lap shear strengths are already in the range of high performance adhesives and only incremental increases in lap shear strength should be anticipated.

The mechanism by which the adhesive bond forms in both the LCP and thermosetting polyesters has been investigated using SIMS and neutron reflection techniques.[25] These complementary analytical techniques were used to examine the entire range of physical and chemical diffusion distances possible in the aromatic copolyesters. Long range effects could be examined by SIMS while neutron reflection would be able to detect localized interfacial diffusion. The contrast across the interface for the aromatic copolyesters was achieved by observing the interpenetration between thin films of deuterated and protonated copolyesters (Figure 8). From the SIMS examination of the adhesion/welding of the polymer–polymer interface between LCP films, it appears as though the bilayered sample completely homogenizes by ITR within the first hour of annealing at 280°C. Neutron reflectivity studies confirm these results.

Table 1. Properties of Crosslinked Aromatic Copolyesters

Glass Transition Temperature (°C)	225
Weight Loss to 400°C in N_2 (%)	0
Weight Loss to 400°C in Air (%)	0
Char Yield at 600°C (%)	40
Density (g/cm^3)	1.35
Moisture Pick-up (wt%)	0.3
Dielectric Constant (25°C, 1 MHz)	4.7

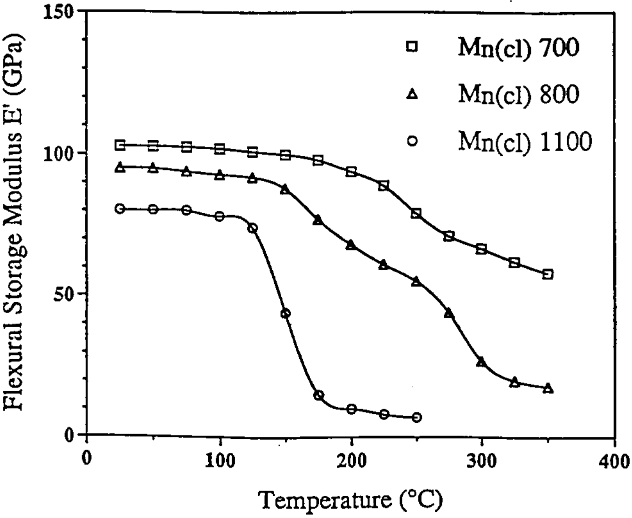

Figure 7. DMA spectra of carbon fiber composites with an aromatic copolyester matrix as a function of crosslink density.

The degree of interpenetration was measured for thin cured aromatic copolyester thermosets via the same technique described above for the LCP bilayered films. No observable changes in SIMS depth profile were observed with annealing after 10 hours at 280°C. Since the depth resolution of SIMS is 500Å, any changes in the polymer–polymer interface must occur over lengths scales less than 500Å. Neutron reflection data after 11 hours at 280°C suggests that the actual amount of interpenetration is less than 300Å.

Interpretation of the SIMS and neutron reflection data for the welding of two cured aromatic copolyester thermoset films is much less ambiguous than for LCP thin film welding. Since the individual films were cured into infinite molecular weight networks prior to joining and annealing, physical diffusion of individual polymer chains or large fragments across the interface would not be possible. Thus, the only mechanism available for adhesion across the polymer–polymer interface would be localized interdiffusion through rapid high temperature ITR.

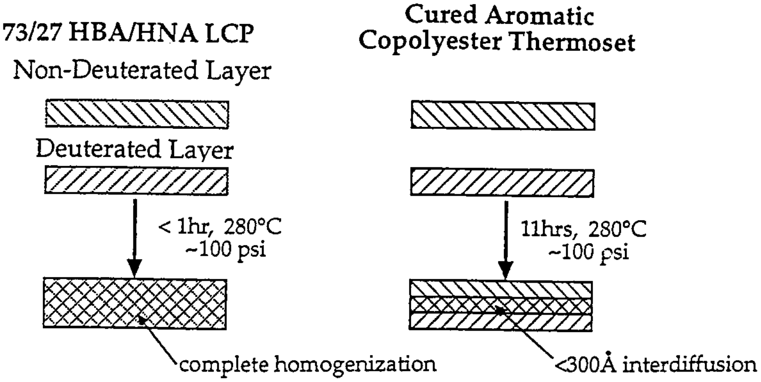

Figure 8. Schematic of the interdiffusion of chains of (a) 73/27 d-HBA/d-HNA and 73/27 HBA/HNA and (b) d-crosslinkable aromatic copolyester and crosslinkable aromatic copolyester upon anneal at 280°C.

CONCURRENT STUDIES ON PROCESSING OF THE POLYESTERS

At present we are actively pursuing several additional projects which have grown out of this program on ITR. These include 1) the design of aliphatic-aromatic copolyesters which can be cured at much lower temperatures, 2) demonstration of a continuous process for fabricating consolidated articles by ITR, and 3) fabrication of advanced microelectronic devices using ITR. Progress in these three areas is briefly summarized below.

Low Temperature Curing

We have recently demonstrated that we can prepare crosslinked aliphatic-aromatic copolyesters starting with lower cost monomers which can be cured at 200°C. Some of these results have just been reported in the literature[26] and will not be discussed in any detail other than to note that for large scale commercial use it is more important to reduce both the cost of the oligomers as well as to lower the cure temperature from 300°C to 200°C.

Continuous Processing

One of the important advantages of ITR in solid state processing of cured polyesters is the potential for continuous processing of coatings and films. We are currently exploring the use of oligomeric mixtures to continuously coat yarns or fabric followed by continuous curing of the coating. For example, a carbon fiber fabric or yarn can be impregnated with the melt to the appropriate concentration and curing carried out in a continuous process with the acetic acid by-product collected separately. Consolidation of the cured stacked composite lamina would be carried out by heating under pressure using ITR.

Design of Novel Multichip Module Laminates

The consolidation of a number of high-density metal circuit containing laminates into a multilevel package can be achieved using the foamed crosslinked polyester laminated onto a LCP carrier film. Polyesters are known for their good self-adhesion and we have observed with TEM that bonding at the interface between a 73/27 HBA/HNA film and the crosslinked aromatic/aliphatic polyester is excellent. Our studies have also shown that ordered 73/27 HBA/HNA LCP films can adhere in the solid state (290·°C, 20°C below T_m) via ITR without any loss in dimensional stability. This should greatly improve the chances for good registration between the circuitized lamina.

In this particular project, we have also shown that the dielectric constant of the copolyester can be reduced from 4.7 to a value of only 2.3 by foaming[27] and that we can modify the oligomers to make them photoimageable by incorporating a methacrylic acid glycolate into one of the oligomers. This aromatic/aliphatic photoimageable dielectric has a 15 second photospeed, 16 μm resolution, and good solubility in standard solvents.[28]

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