

# Characterization of the Imidization of the Aromatic Polyimide LARC-160

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## Synopsis

The polyimide resin LARC-160 was prepared from diethyl-3,3',4,4'-benzophenone tetracarboxylate (BTDE), ethyl-5-norbornene-2,3-dicarboxylate (NE), and Jeffamine AP-22. The imidization reactions of NE and BTDE were studied by HPLC, <sup>13</sup>C-NMR, and IR. NE imidizes slowly at 12°C; BTDE imidizes when the resin is heated above 100°C. Both imidization reactions proceed directly to the imide. Neither amic acid is present in significant quantities at any stage of the imidization reactions. The monomer mixture has been stored at 12°C for periods up to 14 months. The effects of resin aging at this temperature on the chemical composition of the resin monomer mixture and the imidized polymer formed on curing were investigated. Aging the resin monomer mixture has the effect of partially advancing the imidization reaction. Aging also results in the formation of slightly higher-molecular-weight polyimide chains after curing of the resin at 140 and 180°C. Bisnadimide (BNI) is observed as a major reaction product, regardless of resin age.

## INTRODUCTION

Polyimides with aromatic groups in their backbone have generated considerable interest as matrix resins for high-performance composites because of their thermal and thermo-oxidative stability.<sup>1</sup> One processing approach has been to make a predominately linear polyamic acid resin and then to imidize the polymer chain in the cure cycle. A second and more promising approach is to make relatively short imide chains which are encapped with a nadic group.<sup>2</sup> These oligomeric chains are then crosslinked in the postcure cycle through an addition reaction of the end-capping groups at a higher temperature and pressure. LARC-160 is prepared in this manner. Diethyl-3,3',4,4'-benzophenonetetracarboxylate, ethyl-5-norbornene-2,3-dicarboxylate (nadice ester), and a mixture of amines composed primarily of *p,p'*-methylenedianiline are mixed and cured at a temperature between 140 and 200°C, to form the imide. At higher temperatures and pressures, these imide oligomers are crosslinked through an addition reaction involving the nadic end-capping group.

In a preliminary study, Young and Sykes reported that aging the resin at room temperature affected the mechanical properties of cured LARC-160.<sup>3</sup> We have examined the effects of resin aging at 12°C on the chemical composition of the resin monomer mixture and the imidized polymer formed on curing. Changes in the chemistry of the monomer mixture with age were observed and characterized by HPLC and <sup>13</sup>C-NMR. The effect of resin age on the size of the polyimide oligomers, which determines the distance between crosslinks, was determined by HPLC. The imidization reactions of the nadic and benzophenone tetracarboxylate monomers were studied using HPLC, <sup>13</sup>C-NMR, and IR. A revised reaction scheme for LARC-160 polymerization is proposed.

## EXPERIMENTAL

The solventless LARC-160 resin was prepared as prescribed by St. Clair and Jewell using 3,3',4,4'-benzophenone tetracarboxylic anhydride (BTDA), 5-norbornene-2,3-dicarboxylic anhydride (NA), and a commercially available mixture of aromatic amines, Jeffamine AP-22, which is composed primarily of *p,p'*-methylenedianiline (MDA)<sup>2</sup> (see Fig. 1). BTDE, the diethyl ester of BTDA, was prepared by dissolving the anhydride in a 5 M% excess of ethyl alcohol and refluxing for 1 h. NE, the monoethyl ester of NA, was similarly prepared. These mixtures were then cooled and mixed with the appropriate amine molar equivalent of Jeffamine AP-22. The resulting resin mixture was stored in a refrigerator at 12°C.

High-pressure liquid-gel permeation chromatography (HPLC-GPC) was performed on a Waters' Associates Liquid Chromatograph equipped with a model M-6000A chromatography pump, model U6K injector, and a model E 401 differential refractometer.

Two column-solvent systems were used: (a) Samples were dissolved in tetrahydrofuran (THF), UV grade, from Burdick and Jackson, then eluted on a four-column bank consisting of two 500 Å and two 100 Å  $\mu$ -Styragel columns; or (b) samples were dissolved in UV-grade chloroform, also from Burdick and Jackson, and eluted on a five-column bank consisting of one 10<sup>3</sup> Å, two 500 Å and two 100 Å  $\mu$ -Styragel columns.

Carbon 13 nuclear magnetic resonance (<sup>13</sup>C-NMR) studies were done on a Varian FT-80A NMR spectrometer. Samples of the resin were dissolved in DMSO-*d*<sub>6</sub>, with TMS as an internal standard. A spectral width of 5000 Hz was used.

<sup>13</sup>C chemical shift assignments of the carbonyl resonances of BTDE and NE were made by comparison with the monomers and the following model compounds: 3-[(phenylamino)carbonyl]bicyclo[2.2.1]hept-5-ene-2-carboxylic acid; 2-[(phenylamino)carbonyl]benzoic acid; *N*-phenyl-5-norbornene-2,3-dicarboximide; *N,N'*-(methylenedi-*p*-phenylene)di-5-norbornene-2,3-dicarboximide (bisnadimide, or BNI); and *p,p'*-methylenedianiline (MDA). These compounds were supplied by NASA-Langley Research Center.

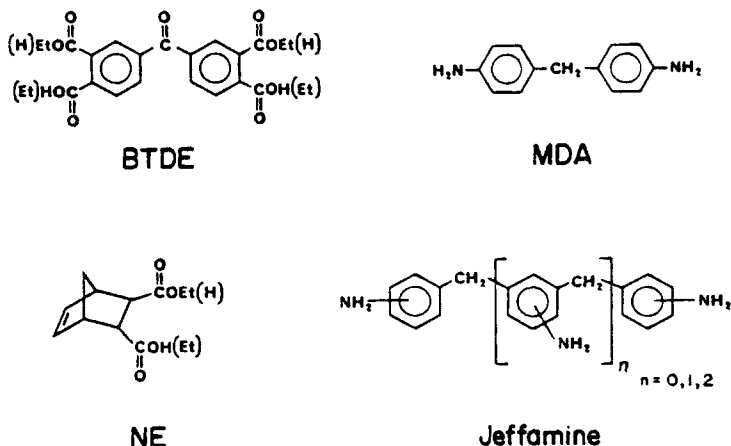


Fig. 1. LARC-160 monomers: BTDE = benzophenone tetracarboxylate diethyl ester; NE = ethyl-5-norbornene 2,3-dicarboxylate; MDA = *p,p'*-methylenedianiline = Jeffamine,  $n = 0$ ; Jef = Jeffamine, where  $n = 0, 1, 2$ .

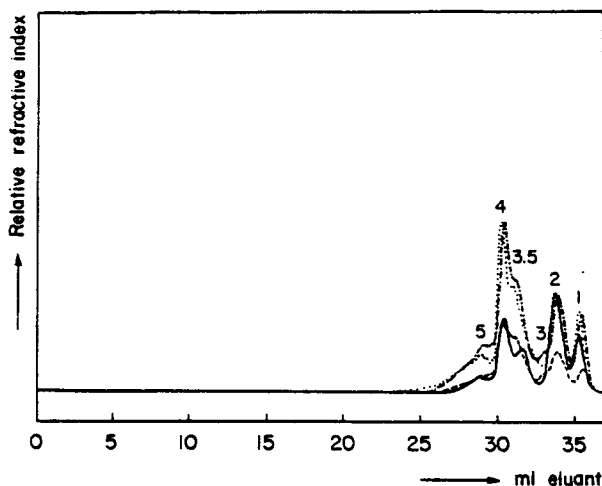


Fig. 2. LARC-160 monomer mixture, "cool mix," 0.2% in THF, eluted from a  $2 \times 500 \text{ \AA} + 2 \times 100 \text{ \AA}$  column bank after the resin was stored at  $12^\circ\text{C}$  for the indicated number of days. (—) day 1, (.....) day 28, (---) day 53, (---) day 106.

A Perkin-Elmer 337 grating infrared spectrophotometer was used for IR studies. Films of fresh resin were prepared on KBr plates, and the same sample was taken through a given cure cycle. IR spectra were taken of the fresh resin and at selected points along the cure cycle.

## RESULTS

### Effect of Age on the Resin Monomer Mixture

The freshly prepared monomer resin mixture was stored at  $12^\circ\text{C}$  in air. Aging of the resin was monitored by HPLC (Fig. 2, Table I). Peaks were assigned according to the elution volumes of the respective monomeric species and verified by spiking resin samples with the monomer. Weight percent values were corrected for differences in the differential refractive index as a function of concentration for each monomer species. A composite value for the oligomers was estimated based on the experimentally determined values for the monomers.

TABLE I  
HPLC Analysis of Aging LARC-160 Monomer Mixture, Cool Mix<sup>a</sup>

Peak	Species	$V_e$ ( $\pm 0.1$ mL)	Weight % after $n$ days at $12^\circ\text{C}$								
			$n = 1$	7	14	28	53	106	287	377	
1	NE	35.2	31	28	26	22	14	13	13	0	
2	Jeffamine, $n = 0$	33.6	21	15	13	12	10	12	9	4 <sup>b</sup>	
3	Nadimide <sup>c</sup>	33.4	—	—	—	9	8	8	15	33 <sup>b</sup>	
3.5	Jeffamine, $n = 1$	31.3	9	5	9	8	9	9	6	1 <sup>b</sup>	
4	BTDE	30.3	33	38	39	40	43	43	46	49	
5	Imide	28.9	6	13	13	10	16	15	13	13	

<sup>a</sup> 0.2% wt/wt in THF; two  $500 \text{ \AA}$  + two  $100 \text{ \AA}$   $\mu$ -Styragel columns.

<sup>b</sup> Peaks 2, 3, and 3.5 are inseparable. Jeffamine peaks are estimated based on the theoretical amount of Jeffamine left, assuming no BTDE has reacted.

<sup>c</sup> In the unpolymerized mixture, both NI and BNI elute at this volume.

As can be seen in Table I, the nadic group reacted with time, even at subambient storage temperatures. The major product of this low-temperature reaction was nadimide, the imides formed from the reaction of one MDA with one NE (NI) and one MDA with two NE (BNI). The presence of nadimide was established by comparison of the HPLC spectra of aged resin and a sample enriched with NI + BNI. Nadimide was first observed in four-week-old resin, and it continued to increase in quantity with resin age throughout the study until, after 377 days at 12°C, all of the nadic groups had imidized (Table I). <sup>13</sup>C-NMR data, which are presented below, also show that after 14 months virtually all of the nadic groups are imidized.

In contrast to NE, BTDE did not imidize at 12°C. An exact determination of the change in the wt % of BTDE was made difficult because the trifunctional amine in Jeffamine (peak 3.5) eluted as a shoulder on the BTDE peak (peak 4). Complete separation of the two components was not possible on the four columns used. Measurement of the relative contribution of each of these two components was subject to error as shown by the variation in wt % reported for these two species. Determining the area of the BTDE peak was further complicated by the presence of the amic acid of the nadic monomer which eluted at about this volume. Additionally, some of the lower-molecular-weight imides formed by the reaction between one NE and the tri- ( $n = 1$ ) or tetra- ( $n = 2$ ) functional Jeffamine overlap and increasingly contribute to this peak area with resin age.

A low-molecular-weight imide (peak 5) was formed when the resin monomer mixture was prepared. Its weight percent increased with time. The low-molecular-weight imide is thought to be a mixture of higher-molecular-weight reaction products between the nadic ester and the tri- and tetrafunctional amines (for example, NE<sub>2</sub>-Jeffamine,  $n = 2$ ). Evidence will be presented later that these short imides are incorporated into longer chains during curing.

The data presented above were obtained on monomers mixed at ~50°C, the temperature at which Jeffamine is just fluid enough to ensure proper mixing with

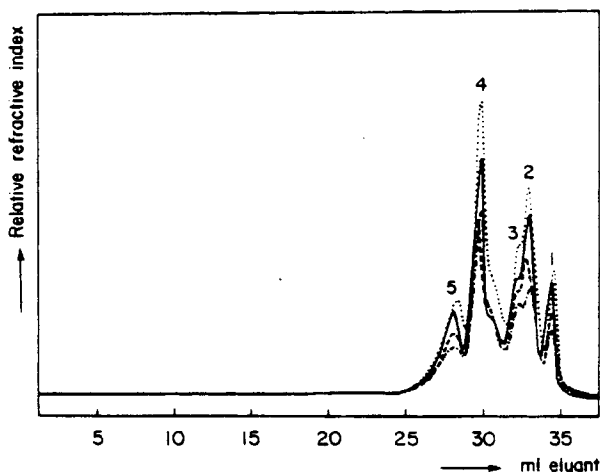


Fig. 3. LARC-160 monomer mixture, "warm mix," 0.2% in THF, eluted from a  $2 \times 500 \text{ \AA} + 2 \times 100 \text{ \AA}$  column bank after resin was stored at 12°C for the indicated number of days. (—) resin, day 1; (---) resin, day 6; (.....) resin, day 13; (-.-) resin, day 40.

TABLE II  
HPLC Analysis of Aging LARC-160 Monomer Mixture, Warm Mix<sup>a</sup>

Peak	Species	$V_e (\pm 0.1 \text{ mL})$	Weight % after $n$ days at 12°C					
			$n = 1$	6	13	19	34	40
1	Nadic ester	35.2	17	16	15	14	12	13
2	Jeffamine, $n = 0$	33.6	13	13	13	12	11	10
3	Nadimide <sup>b</sup>	33.4	13	15	13	14	17	17
3.5	Jeffamine, $n = 1$	31.3	6	6	5	6	4	9
4	BDTE	30.3	31	32	35	36	37	34
5	Imide	28.9	20	19	18	20	19	16

<sup>a</sup> Samples were 0.2% wt/wt in THF; two 500 Å + two 100 Å  $\mu$ -Styragel columns.

<sup>b</sup> In the unpolymerized mixture, both NI and BNI elute at this volume.

the esters. When warmer mixing temperatures were used ( $\geq 80^\circ\text{C}$ ), a monomer resin mixture resembling aged, "cold-mixed" resin was obtained (Fig. 3, Table II). In fact, about the same degree of nadic imidization as measured by nadimide formation was observed in the "warm-mixed," day-old monomer resin mixture as in the aged, "cold-mixed" resin which had been stored eight months. The warm-mixed resin also contained more of the low-molecular-weight imide (peak 5). The wt % of BTDE remained at or above its originally formulated value of 33%, supporting the view that little if any of it had reacted. (The apparent increase in the wt % of BTDE was likely due to formation of the amic acid of the nadic group and nadic-Jeffamine imides which elute at the same volume.)

These marked differences in the apparent extent of reaction of warm- and

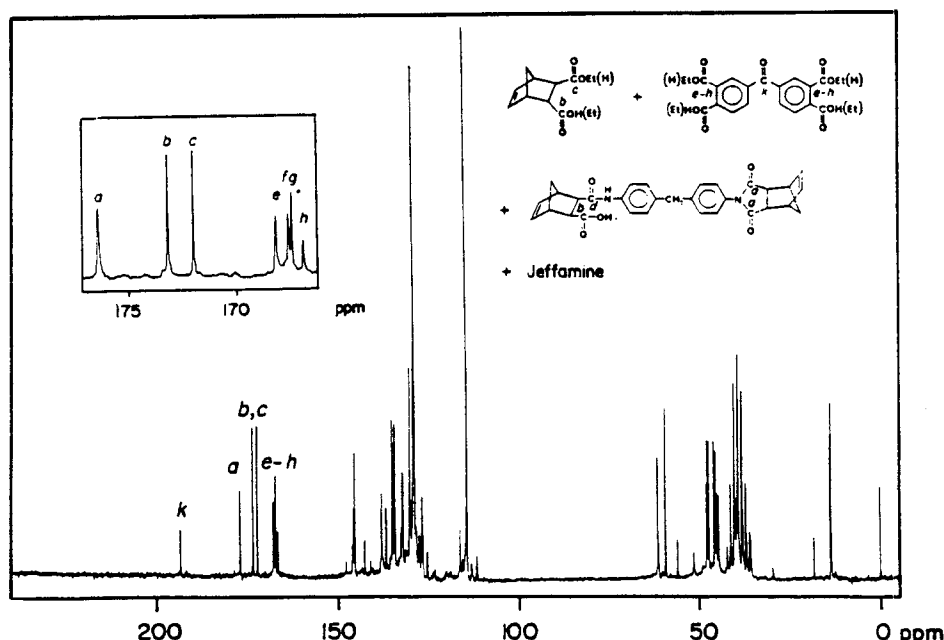


Fig. 4.  $^{13}\text{C}$ -NMR spectrum of LARC-160 monomer mixture immediately after mixing. Solvent =  $\text{DMSO}-d_6$ ;  $k$  = benzophenone tetracarboxylate keto carbonyl;  $a$  = nadic imide carbonyl;  $b$  and  $c$  = nadic acid and ester carbonyls;  $e-h$  = benzophenone tetracarboxylic acid and ester carbonyls.  $t = 1/2-3$  h at RT.

cold-mixed resin show that the monomer resin mixture is sensitive to preparation and storage conditions. For composite preparation, the resin is warmed slightly to achieve proper impregnation of the composite fibers. The actual time and temperature of this prepregging operation can apparently have an effect on the extent of the reaction or "age" of the resin and on resin properties in subsequent curing steps.

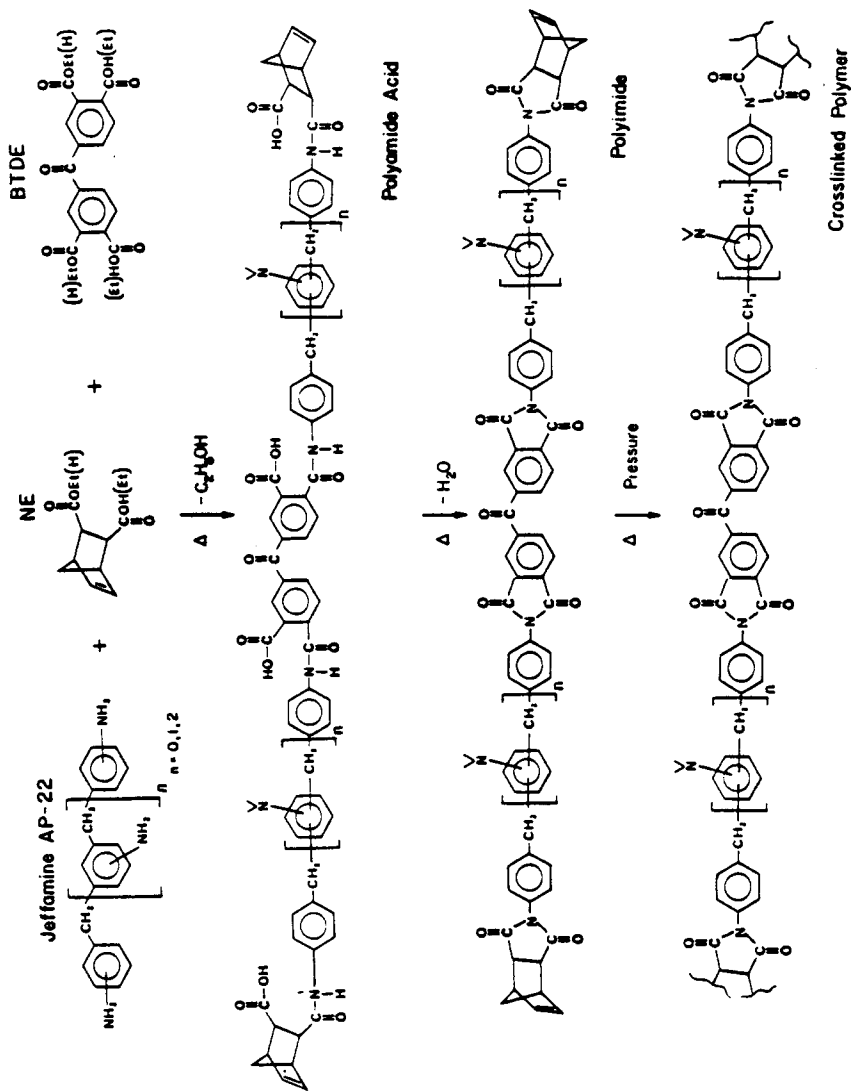
In order to examine the imidization reaction of the LARC-160 resin more explicitly, a  $^{13}\text{C}$ -NMR study of the carbonyl absorption peaks of the aging resin was undertaken. A fresh batch of resin was prepared and mixed warm (with both esters and amines at  $80^\circ\text{C}$ ). Samples of this resin were dissolved in  $\text{DMSO-}d_6$  at different ages for  $^{13}\text{C}$ -NMR analysis.

As can be seen in Figure 4, examination of the nadic carbonyl resonances indicates that nadimide (177 ppm), designated *a*, was present even in this initial sample. The nadic ester and acid peaks (173.3 and 172 ppm), *b* and *c*, were also present. No nadic amide (169.8 ppm), *d*, could be observed. However, after six days at  $12^\circ\text{C}$  (Fig. 5) a small but distinct amide peak, *d*, was observed. The magnitude of this peak remained small and disappeared after 14 months of storage at  $12^\circ\text{C}$  when nadimidization was complete (Fig. 6). Thus, while some amic acid is observed as an intermediate, the reaction clearly favors complete imidization. These findings are contrary to the presumed reaction sequence for LARC-160 (Scheme I),<sup>4</sup> which shows the amic acid forming at low temperatures and the imide appearing only after heat is applied in a dehydration step.

The extent of reaction of the nadic groups with monomer mixture age was determined from the  $^{13}\text{C}$ -NMR data. Although  $^{13}\text{C}$ -NMR does not give quantitative results unless special techniques are employed,<sup>5</sup> an estimate of the amount of nadic carbonyl groups in the acid, ester, amide, and imide forms was made. This analysis was possible because we were only comparing quaternary carbons at the same position on the nadic moiety. In this case,  $T_1$  and NOE effects on these carbons should be similar and their relative intensities of about the same magnitude. The extent of reaction was calculated as follows: all carbonyl functional groups were assumed to have the same intensity. Therefore, the fraction of reacted nadic groups was equal to the imide intensity plus twice the amide intensity (one amide carbonyl plus one acid carbonyl per molecule in this form) divided by the total intensity of all nadic carbonyl groups. The results are shown in Table III.

Our results on the imidization of the nadic group in aging LARC-160 monomer mixtures substantiate the preliminary findings of Young and Sykes who first reported observing BNI in aging LARC monomer mixtures.<sup>3</sup> Imidization of the nadic group in MeOH solutions of PMR monomers at ambient and  $5^\circ\text{C}$  storage temperatures has also been reported.<sup>6</sup> [PMR is a sister resin to LARC in which all of the amine is *p,p'*-MDA (Jeffamine,  $n = 0$ )].<sup>7</sup> Neither of these groups was able to fully characterize the nature of the imide nor observed and followed the increase in imidization over an extended period, as is reported here for LARC-160.

The BTDE monomer was monitored in these same  $^{13}\text{C}$ -NMR studies. Unlike NE, BTDE does not imidize under storage conditions. In the warm-mixed LARC monomer mixture, BTDE peaks were observed at 167.7, 167.1, 166.9, and 166.4 ppm, due to the acid and diester in various combinations (Figs. 4 and 5).



Scheme I.

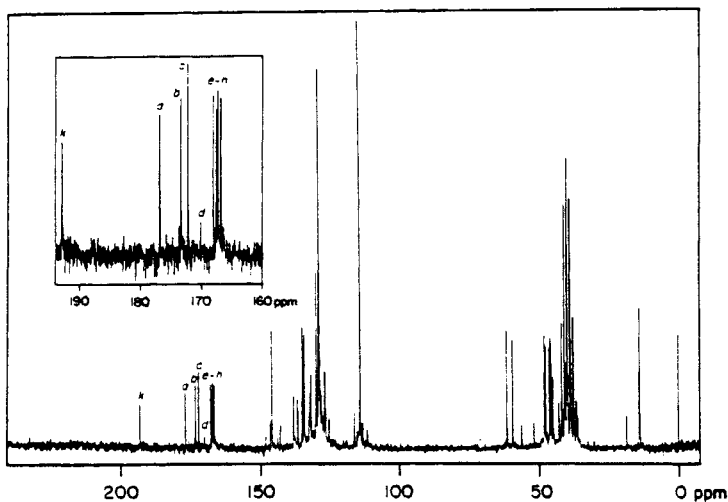


Fig. 5.  $^{13}\text{C}$ -NMR spectrum of LARC-160 monomer mixture after storage for six days at  $12^\circ\text{C}$ .  $d$  = nadic amide carbonyl; other assignments as in Figure 4.

These resonances neither shifted position nor grew in number with resin age. No peak corresponding to the benzophenone tetracarboxylate imide at 166.2 ppm was observed at any age. BTDE appears to be stable over the six-month storage period of this study. These results are in contrast to the reported slow esterification of BTDE to tri- and tetraesters reported for PMR.<sup>8-10</sup> One should note, however, that the cold-mixed resin produced spectra which all contained two additional peaks in the benzophenone tetracarboxylate region (Fig. 6). Spectra of a mixture of tri- and tetrafunctional esters prepared in our laboratory also contained the two peaks in question. Quality control studies on the LARC monomers have shown that small amounts of these esters are often formed during BTDA esterification.<sup>4</sup>

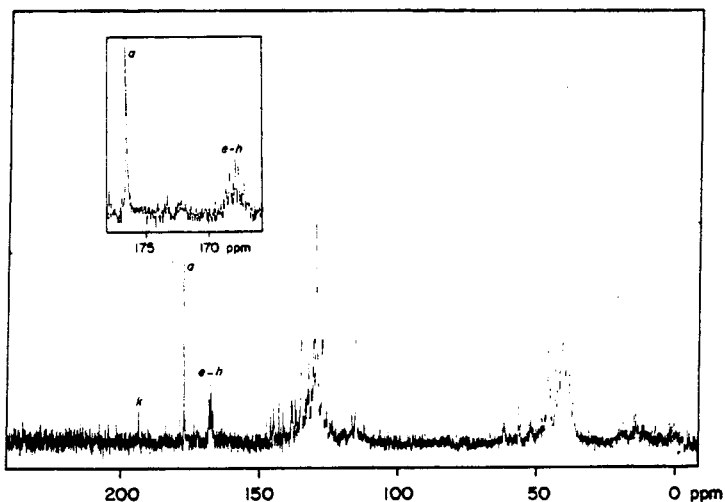


Fig. 6.  $^{13}\text{C}$ -NMR spectrum of LARC-160 monomer mixture after storage for 14 months at  $12^\circ\text{C}$ . Assignments as in Figure 4.



TABLE III  
Percentage of Nadic Groups Reacted With Monomer Mixture Age as Determined from  $^{13}\text{C}$ -NMR Data

Age	% Reacted
1 h	22
7 h	22
15 h	26
6 days	36
13 days	34
40 days	34
6 mo	73
14 mo	100

The lack of additional esterification of BTDE in LARC-160 is not too surprising when one compares the monomer mixture with that of PMR. PMR is stored as an alcohol solution of monomers. The degree of tri- and tetraester formation has been shown to be a function of the amount of that solvent present.<sup>8</sup> LARC, however, is stored as a neat monomer mixture. Therefore, although a small amount of EtOH should be present as a by-product of the nadic imidization reaction, it is insufficient in quantity to cause BTDE esterification.

Our HPLC and  $^{13}\text{C}$ -NMR studies on the effects of age on the monomer mixture indicate that changes in the monomer mixture with age are confined to reactions involving the nadic group. This group slowly imidizes with time. The BTDE group remains unchanged as indicated by both the HPLC and NMR data.

#### The Imidization of Diethyl-3,3',4,4'-benzophenone Tetracarboxylate

Since the nadic group formed an imide directly and BTDE did not react at low temperatures, the imidization of BTDE was then examined. Was there a distinct polyamic acid stage, or did the BTDE monomer also react directly to form the imide? At what temperature did these reactions take place?

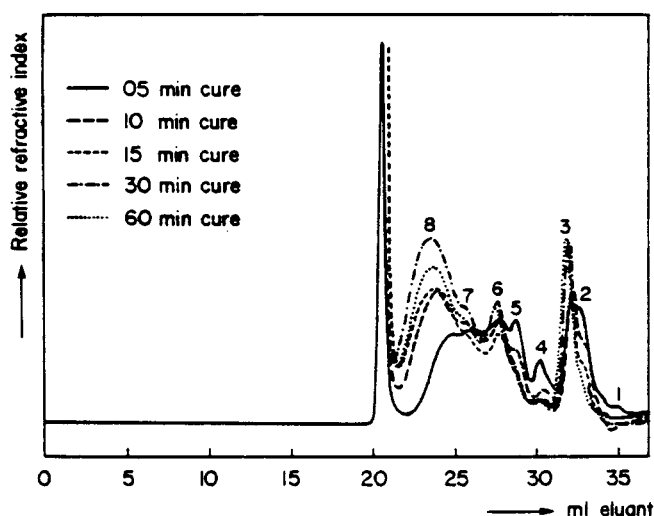


Fig. 7. HPLC spectra of LARC-160 cured at  $180^\circ\text{C}$  for times up to 60 min, 0.2% in THF with polystyrene-51,000 added as an internal standard, eluted from a bank of  $2 \times 500 \text{ \AA} + 2 \times 100 \text{ \AA}$   $\mu$ -Styragel columns.

TABLE IV  
 HPLC Analysis of "Warm-Mixed" LARC-160 After Various Cure Times at 180°C<sup>a</sup>

Peak	Species	$V_e$ ( $\pm 0.1$ mL)	Weight % after $x$ minutes at 180°C						
			$x = 0$	5	10	15	20	30	60
1	Nadic ester	35.2	16	2	—	—	—	—	—
2	Jeffamine, $n = 0$	33.6	13	5	4	3	3	2	1
3	Bisnadimide	33.4	15	10	15	14	15	18	17
3.5	Jeffamine, $n = 1$	31.3	6	—	—	—	—	—	—
4	BTDE	30.3	33	7	5	3	3	3	2
5	Imide	28.7	17	21	8	6	4	5	5
6	Polymer 1	27.8	—	20	14	16	14	13	14
7	Polymer 2	25.5	—	19	17	16	13	12	14
8	Polymer 3	23.9	—	16	34	46	48	47	48

<sup>a</sup> 0.2% wt/wt in THF; two 500 Å + two 100 Å  $\mu$ -Styragel columns.

Fresh, "warm-mixed" resin was cured at 180°C. The degree of imidization as a function of cure time at 180° was monitored by both <sup>13</sup>C-NMR to study the cure reaction and by HPLC to monitor oligomer distribution (Fig. 7, Table IV). Within 15 min at this temperature, the monomers and the low-molecular-weight imide (peaks 1, 2, 4, and 5) appeared to have reacted. After 15 min, changes continued to occur as the shorter oligomers (peaks 6 and 7) reacted to form higher-molecular-weight polymers. Examination of Figure 7 shows a gradual shift in the elution volume of peak 8 to lower values, corresponding to a higher average molecular weight. After 30 min of exposure to this cure temperature, material insoluble in THF began to be formed. The amount of this insoluble high-molecular-weight polymer increased with cure time.

Since BTDE had already completely imidized after 15 min at 180°C, this reaction was followed at several lower temperatures to look for the expected amide intermediate in the imidization process. Table V is a summary of the <sup>13</sup>C-NMR results for the carbonyl shifts. In the benzophenone carbonyl region, one first observes the disappearance of the ester/acid peaks at 166.9 ppm (*g*) and 167.6 ppm (*e*), as the amide at 166.3 ppm (*i*) and the imide at 166.2 ppm (*j*) form. Finally, all peaks in this region (*e-i*) collapse into the imide peak (*j*). The amide peak (*i*) is never observed without the simultaneous presence of the imide peak

 TABLE V  
<sup>13</sup>C-NMR Shifts of Observed Carbonyl Carbons of LARC-160 as a Function of Cure Time and Temperature<sup>a</sup>

Cure temp., °C	Cure time, min	<i>a</i>	<i>b</i>	<i>c</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>
105	60	176.70			167.64	167.12	166.87	166.39	166.26	166.22
105	120	176.64				167.04		166.40	166.32	166.19
125	15	176.74	173.12	171.94	167.65	167.11	166.88	166.38		
125	30	176.64			167.57	167.07	166.81	166.42	166.34	166.23
180	5	176.70			167.59	167.04		166.40	166.33	166.19
180	10	176.61							166.32	166.18
180	30	176.63								166.19

<sup>a</sup> Carbons *a-h* assigned as in Figure 4; *i* = transient benzophenone tetracarboxylate amide; *j* = benzophenone tetracarboxylate imide.

(j), suggesting that the amide is a transient intermediate in the imidization reaction rather than an isolable polymeric species.

The fact that imidization of the nadic and benzophenone tetracarboxylic monomers occurs at two widely different rates and temperatures was confirmed by IR studies. For such studies, a sample was prepared as a thin film between two salt plates. Each sample was run without curing, and then the plates were cured for measured amounts of time and additional spectra taken. Once the imide IR absorbance had become constant, the cure temperature was raised on the same sample and the effect of further curing on the sample was observed.

The imide IR absorption peak has been reported<sup>11</sup> to occur between 1810 and 1775  $\text{cm}^{-1}$ . We observed the imide peak at 1790  $\text{cm}^{-1}$  in LARC-160. In the fresh resin, the amount of imidization, as measured by the intensity of this peak, was negligible. As the sample cured, the peak emerged as a shoulder on the broader 1730–1700  $\text{cm}^{-1}$  carbonyl stretch (Fig. 8).

The percentage of imidization was calculated using the equation<sup>12</sup>

$$\text{Percentage imidization} = \frac{\left[ \frac{A(1)}{A(2)} \right]_t - \left[ \frac{A(1)}{A(2)} \right]_{t=0}}{\left[ \frac{A(1)}{A(2)} \right]_{t=\infty} - \left[ \frac{A(1)}{A(2)} \right]_{t=0}}$$

where  $A(1)$  is absorbance of imide peak at 1790  $\text{cm}^{-1}$ ,  $A(2)$  is absorbance of standard reference peak at 1490  $\text{cm}^{-1}$ , and  $t = \infty$  was taken as the time beyond which no further changes in the imide peak were observed at 220°C.

No imidization was observed in the resin before heating. When the sample was heated at 70°C for up to 660 min, the imide peak grew to approximately 40% of its final size. The sample was then heated at 180° for up to 360 min. This second cure stage brought about a significant increase in the amount of imidization, to approximately 85% of the final imidization. The sample was then cured at 220°C for up to 330 min. The amount of imidization increased slightly, in-

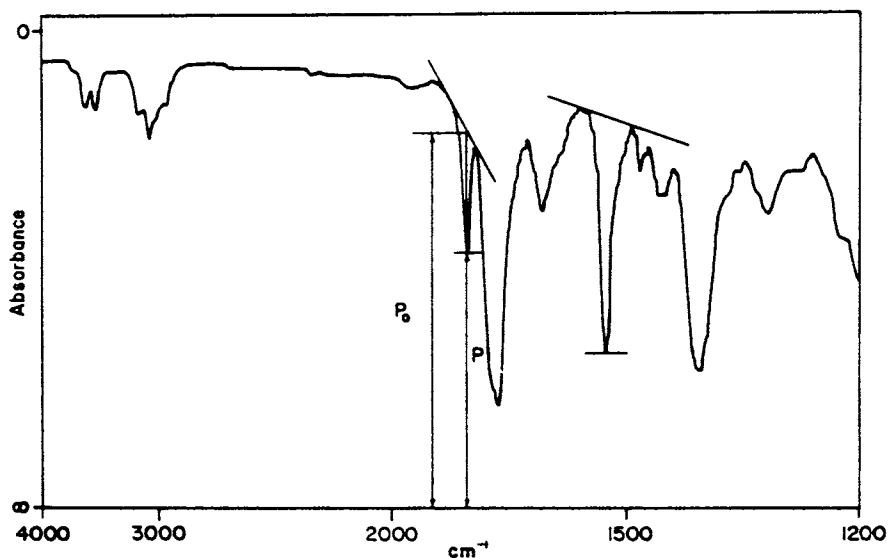


Fig. 8. Infrared spectrum of fully imidized LARC-160 after curing 11 h at 70°, 6 h at 180°, and 2 h at 220°C.

TABLE VI  
Quantitative Analysis of Infrared Spectra of LARC-160 Resin Percent Imidization Versus Cure Time

Cure time, min	Cure temp., °C	% Imidization
0	70	0
10	70	-0.87
20	70	1.5
40	70	5.1
60	70	5.1
90	70	10
120	70	18
180	70	18
300	70	23
420	70	31
540	70	46
660	70	37
840	180	85
960	180	83
1020	180	83
1050	220	94
1110	220	89
1170	220	89
1290	220	99
1350	220	100

dicating that the imidization reaction was not quite complete after curing at 180°C (Table VI). As shown in Table VI, slightly less than one-half of the imide is formed below 100°C, consistent with the hypothesis that only the nadic group, which represents 48% of the carbonyl carbon in the monomer mixture, is reacting at this lower (70°) temperature. The remainder of the imidization, which involves BTDE, takes place at the higher temperature (180°).

An absorption band at 1850  $\text{cm}^{-1}$  at temperatures  $\geq 120^\circ\text{C}$  has been reported

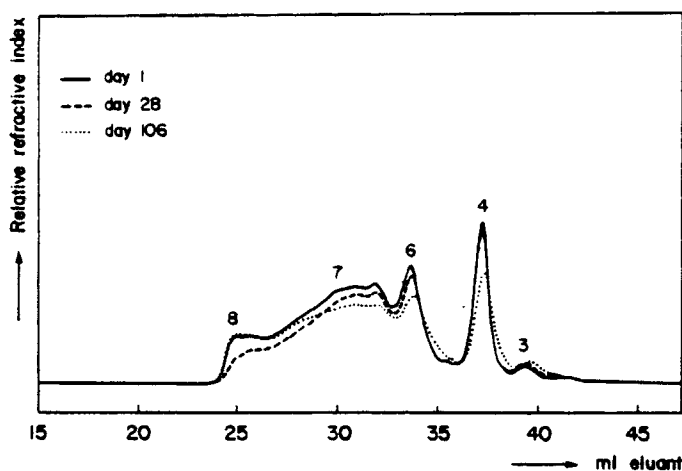


Fig. 9. HPLC spectra of LARC-160 cured at 180°C/1 h from aging monomer mixture; 0.2% in  $\text{CHCl}_3$ , eluted from a five-column bank consisting of  $1 \times 10^3 \text{ \AA}$ ,  $2 \times 500 \text{ \AA}$ , and  $2 \times 100 \text{ \AA}$   $\mu$ -Styragel columns. The monomer mixture was stored at 12°C for the indicated number of days before being cured.

and attributed to anhydride formation as an initial competing reaction to imidization in the related PMR system.<sup>13-15</sup> We do not observe any absorbance in this region for the curing LARC resin. Furthermore, the <sup>13</sup>C-NMR experiments on samples cured at 180° did not detect any anhydride for either the nadic (172.3 ppm) or benzophenone tetracarboxylate (162.4 ppm) carbonyl groups (Table V).

The IR experiments substantiate the <sup>13</sup>C-NMR and HPLC data which indicate that imidization occurs in two stages: first, low-temperature imidization of the nadic moiety forming the end-capped amines and bisnadimide; and second, at temperatures over 100°C, imidization of the benzophenone tetracarboxylate monomer.

In solution, polyimides are formed via the low-temperature polymerization to the polyamic acid, which imidizes upon the application of heat. Polymerization of solventless LARC monomeric resin has been assumed to follow the same reaction sequence.<sup>4</sup> However, based on the above evidence for the formation of bisnadimide, even at subambient temperatures, and the observation of the benzophenone tetracarboxyl amic acid only as a transient intermediate, we believe Scheme II is a more accurate representation of the imidization reaction sequence for LARC-160 polymerization.

### The Effect of Resin Age on the Cured Polymer

The major effect of age on the LARC-160 monomer mixture appears to be the preferential reaction of NE with the amine mixture. The consequences of this partial advancement on the cured resin product will be considered next.

The effect of resin aging on the length of the oligomeric chains was examined. Curing reactions under constant conditions were performed at intervals as the "cold-mixed" LARC-160 monomer resin mixture aged. Samples of the aging monomer resin mixture were cured at either 140 or 180° for 1 h on the same day that the monomer mixture was examined by HPLC.

As can be seen by Figure 9 and Table VII, HPLC analysis of the polymeric species formed at 180° shows a small but noticeable shift toward higher molecular weight as the resin ages. The elution volumes of the three polymeric segments designated polymer 1, 2, and 3 correspond to elution volumes for polystyrenes of molecular weight 1000, 3,000–20,000 and >20,000, respectively. Peak 5, which has been attributed to unfully end-capped imides (see discussion of monomer mixture results), is not present in these cured samples, and the wt % of peak 3, which was attributed to BNI + NI, is reduced. During the curing process, the

TABLE VII  
HPLC Analysis of Aging LARC-160 Cured at 180° for 1 h<sup>a</sup>

Peak	Species	$V_e$ ( $\pm 0.1$ mL)	Weight % after $n$ days at 12°C			
			$n = 1$	28	53	106
4	BTDE	40	2.9	4.7	2.7	2.6
3	Bisnadimide	37.7	22.1	22.9	21.3	19.9
6	Polymer 1	34.1	17.9	19.8	16.8	16.7
7	Polymer 2	30	48.4	44.4	48.2	48.0
8	Polymer 3	25.5	8.7	8.1	11.0	12.8

<sup>a</sup> 0.2% wt/wt in CHCl<sub>3</sub>; one 10<sup>3</sup> Å + two 500 Å + two 100 Å  $\mu$ -Styragel columns.



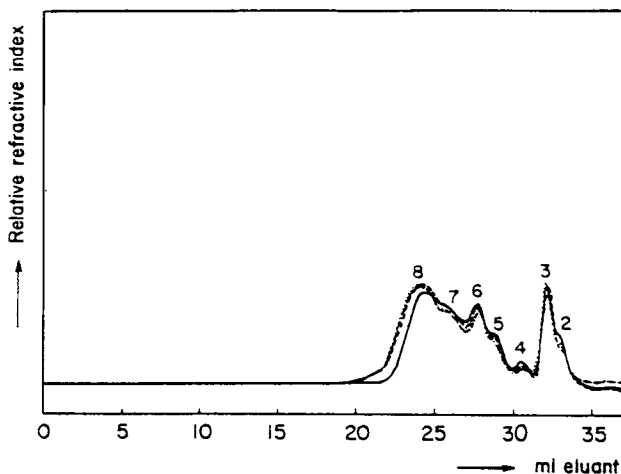


Fig. 10. HPLC spectra of LARC-160 cured at 140°/1 h from aging monomer mixture, 0.2% in THF, eluted from a bank of 2 × 500 Å + 2 × 100 Å μ-styragel columns. The monomer mixture was stored at 12°C for the indicated number of days before being cured.

incompletely end-capped nadimides are incorporated into longer chains. BNI, capped at both ends, is unable to react further and remains as a low-molecular-weight component in the polymer system. BNI is observed as a major reaction product in the cured polymer regardless of resin age. The amount of BNI present in the resin aged 106 days and cured at 180° (approximately 20% by weight, as shown in Table VII) corresponds to 43% of the original nadic ester. Similarly high concentrations of BNI were observed in all cured polymer samples. Tying up this amount of NE as BNI results in polyimides containing an average of two rather than one BTDE unit per oligomer. Results for ages greater than 106 days are not shown because the amount of insoluble material increased with age so that these polymers could not be examined by the solution methods available to us.

A similar shift toward higher molecular weight of the cured product with increasing monomer mixture age is observed at a 140° cure temperature. Changes in the polymer cured at 140°C for 1 h as a function of age can be seen in the amounts of residual Jeffamine and BTDE and the higher-molecular-weight species designated imide and polymer 3. The elution volume of the low-molecular-weight imide corresponds to the elution volume of polystyrene of mo-

TABLE VIII  
HPLC Analysis of Aging LARC-160 Cured at 140° for 1 h<sup>a</sup>

Peak	Species	$V_e$ (± 0.1 mL)	Weight % after $n$ days at 12°C						
			$n = 1$	4	7	14	28	53	106
2	Jeffamine, $n = 0$	33.0	4	3	3	3	3	2	2
3	Bisnadimide	32.3	19	18	17	16	16	17	17
4	BTDE	30.5	5	6	6	6	5	5	2
5	Imide	28.7	8	8	8	7	8	6	5
6	Polymer 1	27.8	18	16	17	15	15	15	16
7	Polymer 2	25.5	13	16	17	15	17	14	17
8	Polymer 3	24.3	33	34	34	38	38	43	41

<sup>a</sup> 0.2% wt/wt in THF; two 500 Å + two 100 Å μ-Styragel columns.

lecular weight 800; polymers 1, 2, and 3 correspond to polystyrene molecular weights of 1000, 2500, and 5000, respectively. BNI is a major reaction product whose concentration appears to be independent of resin age. LARC polymer is not completely cured after 1 h at 140°C, as shown by the existence of BTDE and Jeffamine peaks in the HPLC spectra (Fig. 10, Table VIII) and verified by the presence of unreacted BTDE in the <sup>13</sup>C-NMR spectra. The Jeffamine, BTDE, and imide peak areas all decrease, and that of polymer 3 (the highest-molecular-weight species) increases with the age of the resin. These results show that aging the resin has the effect of partially advancing the reaction since more polymer and less Jeffamine and BTDE are observed under identical cure conditions with increasing age of the monomer mixture. Furthermore, aging the monomer resin mixture leads to the formation of slightly higher-molecular-weight polyimide chains after curing at 140 and 180°.

The increase in degree of cure at a given cure time and temperature for aged LARC monomer resin mixture is in contrast to effects of resin aging in the PMR system. Lauver has found that PMR resins containing the BTTE products formed during storage of alcohol solutions of PMR prepolymer require longer and higher temperatures to imidize.<sup>8-10</sup> In the LARC-160 system, however, we have shown that the nadic group reacts with time but that BTDE remains stable under the conditions of our experiments. The partial preimidization of the nadic group produces an advanced reaction state for the aged resin; and when identical cure times are used for aged and fresh monomer mixtures, the older mixture has a higher average cured molecular weight.

## CONCLUSIONS

The composition of LARC-160 resin monomer mixture changes during aging at 12°C. The major effect of resin age is the formation of BNI and the advancement of the nadimization reaction.

The NE and BTDE monomers imidize under different conditions. NE imidizes at 12° over a period of weeks and is completely imidized in a few minutes at 125°. No BTDE imidization was observed at 12°. Imidization of BTDE at 125° requires several hours but is complete in 10 min at 180°.

Both NE and BTDE imidization reactions proceed directly to the imide. Neither amide is present in significant quantities during any stage of the imidization reaction and is not a stable intermediate.

Aging the monomer resin mixture leads to the formation of slightly higher-molecular-weight polyimide chains after curing at 140 and 180°.

BNI is a major product of polymerization of LARC-160, regardless of resin age.

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