

## TRANSIMIDIZATION IN THERMOPLASTIC POLYIMIDES\*

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**Abstract** In order to improve the processability in thermoplastic polyimides, a new method, termed the "reactive plasticizer" approach, has been proposed. This method uses a small amount (5~15 mol%) of a less activated, weak nucleophilic diamine *co*-monomer as a "reactive plasticizer" to obtain copolyimide resins which possess relatively low viscosity at low temperatures and can be readily processed through the autoclave cycle at low pressures. During a high temperature treatment, the reactive plasticizers join the reaction to form high molecular weight copolyimides, and the preferred material properties are thus achieved. The most effective reactive plasticizer is aromatic heterocyclic diamines, such as 2, 6-diaminopyridine diamine (DAP), and the transimidization involved with a reactive plasticizer has been proposed to play a major role for the success of this approach. In order to understand the transimidization mechanism, three steps have been taken in this research: first, a copolyimide system of 50% of DAP and 50% 1, 4-bis[4-aminophenoxy]benzene diamine (DODA) with 100% of 2, 2'-bis[4-(3, 4-dicarboxyphenoxy)phenyl] propane dianhydride (Ultem® DA) is prepared. Second, several specifically designed polyimide mixture systems were used, and they consist of two homopolyimides: one is Ultem® DA-DODA, and the other is Ultem® DA-DAP. The third step is to investigate two mixture systems in which Ultem® DA-DODA is mixed with DAP monomer solution and Ultem® DA-DAP is mixed with DODA monomer solution. For all systems, with increasing degree of transimidization upon heat-treatment, the chain structures of the mixtures and their thermal and dynamic mechanical transition behaviors are investigated *via* one-dimensional and two-dimensional nuclear magnetic resonance, differential scanning calorimetry, and dynamic mechanical analysis experiments. Experimental results indicate that in the mixture of two homopolyimides, transimidization takes place much more efficiently in solution than in the melt. For the two mixtures with monomer solutions, the transimidization can only be found in the mixture of Ultem® DAP/DODA system in *p*-chlorophenol, and this process does not effectively occur in the Ultem® DODA/DAP system in *p*-chlorophenol, indicating that free DODA can efficiently attack the imide linkage of Ultem® DA-DAP. The final product resulting from the transimidization in the mixtures is a random copolyimide with a major population of DAP as end groups for the copolymer system.

**Keywords** Transimidization, Thermoplastic polyimides

## INTRODUCTION

Since aromatic polyimides were first synthesized in 1908<sup>[1]</sup>, a great amount of research focusing on them has been carried out. This growing interest results from the material properties of aromatic polyimides, such as excellent thermal and thermo-oxidative stability, good chemical resistance, dimensional stability, and useful mechanical properties. Aromatic polyimides have played an

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important role as high-performance and high-temperature organic materials in the applications of automotive structures, high temperature adhesives, and electrical and electronics materials. Aromatic polyimides have become prominent candidates as composite matrix materials, especially in the aerospace industry.

However, thermoplastic aromatic polyimides usually possess high melt viscosities and high glass transition temperatures ( $T_g$ s), and thus restrict compression molding or melt processing. The good solvent resistance also limits solution processing of these polyimides. As an example, DuPont has developed a thermoplastic polyimide, Avimid® N, synthesized from (6FDA-PPD). This aromatic polyimide has a very high  $T_g$  of  $\sim 370^\circ\text{C}$ , a high level of toughness, and excellent thermooxidative stability. Yet the resin has shown severe processing problems in the fabrication of composites due to its low melt flow and volatile evolution<sup>[2]</sup>. Another example is a semicrystalline polyimide synthesized from (BTDA-DMDA)<sup>[3]</sup>. This resin also shows excellent mechanical properties, in particular its high toughness, and possesses a great potential to be used as a high-performance and high-temperature matrix material in fiber reinforced structural composites. A specific processing route is necessary, which requires that the low molecular weight BTDA-DMDA be processed through the preferred autoclave technique in order to obtain good melt flow. The high molecular weight materials can only be obtained after a high temperature treatment cycle.

Considerable effort has been made to enhance the processability of thermoplastic aromatic polyimides<sup>[4-7]</sup>. One of the attempts utilizes a monomeric solution route, applied to prepare Avimid® K-III prepregs by DuPont<sup>[6]</sup>. In this approach, one reacts a diamine with a much less reactive diethyl-ester diacid rather than the corresponding dianhydride. For this reason, little or no reaction between these two reactants occurs during the preparation of a prepreg solution. Consequently, such a monomeric solution wets surfaces of reinforcing fibers before the polymerization occurs to form a high molecular weight polyimide during the autoclave cycle. Therefore, it facilitates the processing to provide large laminates of excellent quality (less than 0.5% voids) by autoclave molding. Nevertheless, the applicability of this approach is limited to only a few polyimides due to the specific synthesis of the diethyl-ester diacid.

As a widely applicable method to provide enhanced melt flow and consequently better processability of the polyimides, a "reactive plasticizer" approach has been proposed<sup>[8]</sup>. This method involves the preparation of a prepreg solution which contains 100% of the dimethyl-ester form of dianhydrides, 85 ~ 95 mol% of major reactive diamines and 5 ~ 15 mol% of less reactive, deactivated weak nucleophilic diamines as a reactive plasticizer. Early in the autoclave processing cycle at relatively low temperatures, the stoichiometry of a prepreg solution is thus "effectively" offset due to low reactivity of the deactivated diamines. Consequently, only oligomers of the polyimides can be formed and the melt viscosity remains low. The deactivated diamines also function like plasticizers to enhance the oligomer melt flow. As soon as the temperature at which the deactivated diamines can react with dianhydrides is reached, they participate in the polymerization to restore the stoichiometry and produce high molecular weight copolyimide resins at the end of the processing cycle. A previous study has shown that aromatic heterocyclic diamines are good candidates to be the reactive plasticizers, since the heterocyclic ring itself is a deactivating unit. Among them, 2, 6-diaminopyridine (DAP) is found to be the most effective.

It is speculated that the success of this approach should be attributed to the transimidization reaction involved with the reactive plasticizer upon its incorporation into the chain backbone. This may keep the chemistry alive during the preparation of high molecular weight polyimides. The first transimidization reaction was observed by Spring and Woods in 1945, when they treated phthalimide with excess aqueous methylamine to yield N-methylphthalimide<sup>[9]</sup>. Since then, transimidization has been studied in the systems of an imide monomer and an amine monomer<sup>[10-12]</sup>. Transimidization has also been reported as a polymerization method to prepare

polyimides from bisimide monomers and diamine monomers<sup>[13–15]</sup> or to synthesize segmentally alternating copolyimides by reacting the end-capped oligomeric imides with structurally dissimilar amine-terminated oligomers<sup>[16]</sup>. In particular, a previous study has shown that bisimides end-capped, hetero-aromatic monoamines, such as, 2-aminopyridine, are very reactive with added nucleophilic amines, and readily undergo the transimidization reaction<sup>[15]</sup>. Consequently, this leads to a speculation of the reactive plasticizer approach, where 2, 6-diaminopyridine (DAP) may also be susceptible to a transimidization by more nucleophilic monomeric, oligomeric or polymeric amines when DAP is incorporated in the chain backbone. Nevertheless, there is no conclusive evidence that the transimidization reaction has taken place in these polyimide systems.

In this study, we attempt to provide conclusive evidence of transimidization in a polyimide system, which is synthesized from 2, 2'-bis[4-(3, 4-dicarboxyphenoxy)phenyl]propane dianhydrides (Ultem<sup>®</sup> DA) and 1, 4-bis[4-aminophenoxy]benzene (DODA) and 2, 6-diaminopyridine (DAP) as diamines (normal and deactivated diamines, respectively). Three systems are prepared: a copolyimide [Ultem<sup>®</sup> DA-DODA-DAP (5/5)] synthesized from Ultem<sup>®</sup> DA with 50 mol% DODA and 50 mol% DAP. A mixture of two homopolyimides (Ultem<sup>®</sup> DA-DODA and Ultem<sup>®</sup> DA-DAP) is also prepared. Finally, both homopolyimides are also mixed with diamine solutions, namely, Ultem<sup>®</sup> DA-DODA mixed with DAP and Ultem<sup>®</sup>-DAP mixed with DODA in *p*-chlorophenol to investigate the transimidization mechanism. The transimidization reaction is activated by heating each system in either the melt or the solution. With developing the degree of transimidization the glass transition behaviors are studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and chain chemical structure changes are followed *via* one-dimensional (1-D) and two-dimensional (2-D) nuclear magnetic resonance (NMR) experiments. Based on this study, we hope to achieve further understanding of the transimidization physico-chemical mechanism.

## EXPERIMENTAL

### Reagents and Solvents

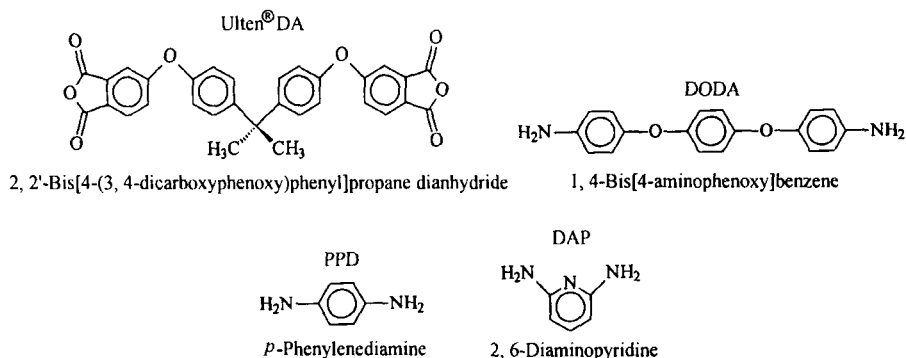


Fig. 1 Monomers and corresponding nomenclatures used in this study

Monomers for this study are shown in Fig. 1. In order for the prepared polyimides to have good solubility and relatively low glass transition temperatures ( $T_g$ s) compared to other thermoplastic aromatic polyimides, a common dianhydride 2, 2'-bis[4-(3, 4-dicarboxyphenoxy)phenyl]propane dianhydride (Ultem<sup>®</sup> DA) was chosen. Ultem<sup>®</sup> DA was provided by General Electric Co. and recrystallized from acetic anhydride and dried at 150 °C under reduced pressure. The reactive diamine used was 1, 4-bis[4-aminophenoxy]benzene (DODA) which was purchased from Chriskev Co. and recrystallized from ethanol. The weak nucleophilic diamine, 2, 6-diaminopyridine (DAP), was chosen, where the pyridine ring itself deactivates the nucleophilicity of the pendant amino

groups. The monomer was purchased from Aldrich Chemical Co. Prior to use, DAP was sublimed under the reduced pressure. Another reactive diamine, PPD, obtained from Aldrich Chemical Co., was distilled under reduced pressure before synthesis. Isoquinoline and *p*-chlorophenol were also distilled under reduced pressure prior to use, and *N*-methyl-2-pyrrolidinone (NMP) was distilled over phosphorous pentoxide. Chloroform and methanol were used as received. All the solvents were purchased from Fisher Scientific Co.

### **Synthesis of Polyimides**

Ultem® DA-DODA-DAP (5/5) copolyimide was prepared *via* one-step polymerization in *p*-chlorophenol. First, in a four-necked resin kettle equipped with an overhead stirrer and nitrogen inlet, DODA (2.5 mmol) and DAP (2.5 mmol) were completely dissolved together in *p*-chlorophenol (20.0 mL), and Ultem® DA (5.0 mmol) was then added to bring the final reaction solids content to ~ 10% (w/w). The reaction mixture was stirred for 3 h at 45°C, and heated gradually to 220°C under dry nitrogen with the addition of isoquinoline (10 drops) at 190°C. The reaction was allowed to proceed at 220°C for an additional 12 h while removing the water released by the imidization reaction. The polymer was isolated by precipitation in methanol in a high-speed blender. The copolyimide was collected by filtration and dried for 2 h at 250°C in a vacuum oven. Ultem® DA-DODA and Ultem® DA-PPD homopolyimides were also prepared *via* one-step polymerization. The procedures were similar to that described above.

For better observation of transimidization, it was desirable to have a high molecular weight Ultem® DA-DAP homopolymer that provides many reactive sites along the chain backbone susceptible to the transimidization reaction. Ultem® DA-DAP homopolyimide was thus prepared *via* melt polymerization. Ultem® DA (5.0 mmol) and DAP (5.0 mmol), mixed well in a mortar, were placed in a two-necked flask equipped with nitrogen inlet and vacuum outlet. The equimolar mixture was slowly heated to the melting point of DAP and kept for 2 h under nitrogen. The mixture was then heated slowly to 250°C and maintained for 1 h under nitrogen. Finally, the reaction mixture was slowly heated to 300~320°C and kept for 1 h under reduced pressure. The solid product was purified by dissolving in NMP, followed by precipitation in methanol with agitation. The polyimide was collected by filtration and dried for 2 h at 250°C in a vacuum oven.

All of the polyimides prepared for this study are amorphous, and only show glass transitions. They are soluble in chloroform, NMP, *m*-cresol, and *p*-chlorophenol.

### **Instrument and Experiments**

To examine complete imidization of samples before and after heat-treatment as well as the transimidization reaction, thermogravimetric analyzer (TA-TGA-2950 at 20°C/min in N<sub>2</sub>) with a Thermal Analyst 2000 system and a Fourier transform infrared spectroscopy (Mattson Galaxy-5000 FTIR) were used.

Viscosity measurements were performed in NMP at 30°C using a Cannon-Ubbelohde 75, A68 viscometer. Intrinsic viscosity of the samples was calculated from flow times which were recorded for the sample solutions with respect to concentrations of 0.50, 0.33, 0.25, and 0.20 g/dL.

Glass transition behaviors were detected using a Seiko DSC 220C. The samples were in the form of powder and 5~15 mg samples were loaded in aluminum pans of the same weight ( $\pm 0.005$  mg). An empty aluminum pan of the same weight was used as the reference. DSC thermograms at a scan rate of 10°C/min in N<sub>2</sub> were obtained after heating the samples at 20°C/min to 270°C, which is well above  $T_g$ s, and holding for one minute followed by quenching into liquid nitrogen to eliminate the previous thermal history. DSC thermograms shown in this paper were normalized for a sample weight of 10 mg.

Dynamic mechanical behavior was examined on a Perkin-Elmer DMA7, which was calibrated by a two-standard temperature calibration using indium and zinc. The film samples were prepared

via a solvent-casting method from chloroform. Measurements were made at a heating rate of 5°C/min in an extension mode, where a static stress of  $1.00 \times 10^5$  Pa, a dynamic stress of  $8.33 \times 10^4$  Pa, and a frequency of 1 Hz were applied.

Most of the NMR spectra were recorded at room temperature on a Varian Gemini-200 MHz spectrometer, and the frequencies were set at 199.9 MHz for  $^1\text{H}$  and 50.3 MHz for  $^{13}\text{C}$ , unless otherwise stated. The 90° pulse width (PW90) calibrations were made for both  $^1\text{H}$  and  $^{13}\text{C}$ . Deuterated chloroform ( $\text{CDCl}_3$ ) was used as the solvent and reference, and its peak was set at 7.24 for  $^1\text{H}$  and 77.0 for  $^{13}\text{C}$ . The sample concentrations were 0.5 ~ 2% ( $\text{g}/\text{cm}^3$ ) for  $^1\text{H}$  and ~10% ( $\text{g}/\text{cm}^3$ ) for  $^{13}\text{C}$ -NMR experiments. Some NMR results were also obtained on a Varian Gemini-300 MHz Spectrometer.

Two-dimensional  $^1\text{H}$ -NMR spectra were recorded at 200 MHz on a Varian Gemini-200 MHz NMR spectrometer at room temperature, using the techniques of correlation spectroscopy (COSY) and nuclear Overhauser exchange spectroscopy (NOESY)<sup>[17-19]</sup>. The sample concentration was either 0.5% or 10% ( $\text{g}/\text{cm}^3$ ) in  $\text{CDCl}_3$ . Both COSY and NOESY experiments were carried out for the aromatic proton region between 6.4 and 8.2. For the NOESY experiments, a mixing time of 200 ms was employed.

## RESULTS AND DISCUSSION

### Transimidization in Ultem® DA-DODA-DAP (5/5) Copolyimide

In order to find evidence of transimidization in a polyimide system, Ultem® DA-DODA-DAP (5/5) copolymer was heat-treated in two different ways to activate a possible transimidization reaction by the amine end groups in the copolyimide. One was to follow the temperature profile of an autoclave molding by placing the copolyimide in a miniclave and heating to 310°C for 3 h under 250 psi of nitrogen pressure. The other was to dissolve the copolyimide in *p*-chlorophenol, and then heat-treat the solution for 24 h at 210°C under a dry nitrogen atmosphere. The polymer was then precipitated in methanol and dried in a vacuum oven.

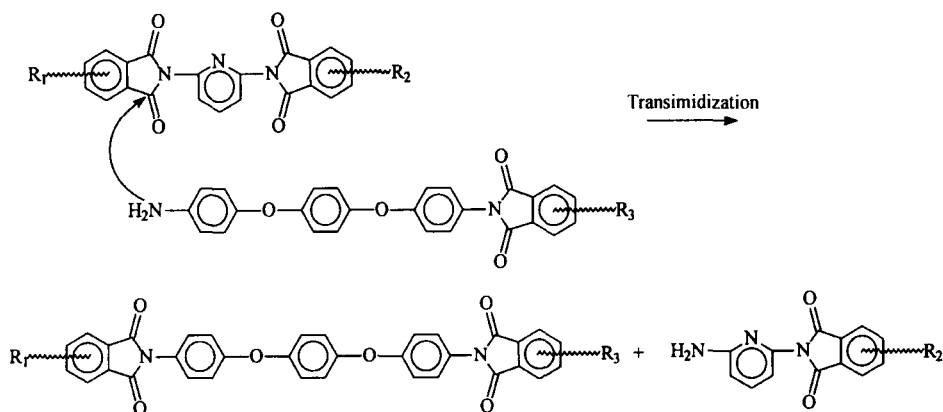


**Fig. 2** Schematic diagram describing the transimidization reaction by a reactive diamine-ended chain onto a DAP-imide linkage

It was speculated that only DAP would be susceptible to transimidization at elevated temperatures when it is incorporated in the chain backbone (Fig. 2), and therefore, the process of transimidization in a random copolyimide would result in a less random distribution of the comonomer sequence. At the completion of transimidization, a random copolyimide would more or less become a block copolyimide<sup>[8]</sup>. As shown in Fig. 3 however, neither the autoclaved nor the solution heat-treated copolymer shows two glass transitions which would be expected with a microphase separated block copolymer behavior. For the solution heat-treated copolyimide a

dramatic decrease in  $T_g$  is observed from the initial value of 211°C to a final value of 197°C. Such a decrease in  $T_g$  is attributed to a decrease of molecular weight in this copolyimide during the heat treatment. This can be confirmed by intrinsic viscosity measurements with the initial copolyimide having a viscosity of 0.67 dL/g and the final heat-treated solution having a viscosity of 0.15 dL/g. On the other hand, the autoclaved copolyimide shows no significant difference in  $T_g$  (only a 2°C increase, see Fig. 3). The NMR results show identical chemical shifts before and after heat treatment. These results indicate that although there may be an occurrence of transimidization to a very minor degree, the final copolymer random sequence is kept.

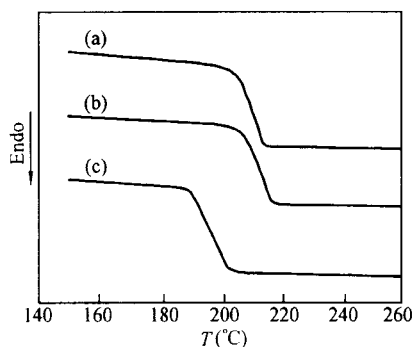


**Fig. 3** DSC thermograms of Ultem® DA-DODA-DAP (5/5) copolyimide (a) before and (b) after autoclaving for 3 h/310°C under  $N_2$  pressure or (c) heat treatment for 24 h/210°C in *p*-chlorophenol

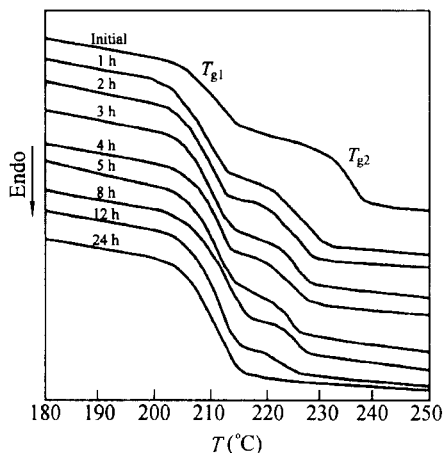


**Fig. 4** DSC thermograms of Ultem® DA-DODA/Ultem® DA-DAP mixture before and after heat treatment at 210°C in *p*-chlorophenol for different times

#### **Transimidization in Ultem® DA-DODA/Ultem® DA-DAP Mixture**

A homogeneous solution mixture of Ultem® DA-DODA and Ultem® DA-DAP homopolyimides in NMP at room temperature was prepared in a 1:1 mole ratio in composition of their repeating units. The mixture was then precipitated in methanol and dried to form solid powder. The initial mixture exhibits two glass transition temperatures (Fig. 4) of  $T_{g1}$  at 211°C and  $T_{g2}$  at 234°C. The lower  $T_{g1}$  is attributed to Ultem® DA-DODA homopolymer and the higher one is the  $T_g$  of Ultem® DA-DAP homopolymer ( $T_{g2}$ ). The mixture was then redissolved in *p*-chlorophenol under nitrogen atmosphere, and heat-treated at 210°C to activate the possible transimidization reaction. At predetermined time intervals during the heat-treatment, equal amounts of the solution were extracted and the resulting polymer was precipitated in methanol in order to examine the glass transition temperature change of the polymer with respect to heat-treatment time. As shown in Fig. 4, the  $T_{g2}$  of the mixture after one hour heat-treatment shows a 10°C decrease, and this decrease continues upon increasing the heat-treatment time. On the other hand,  $T_{g1}$  slightly increases when the heat treatment proceeds. Finally, the two  $T_g$ s merge at 212°C after the mixture is heat-treated for 24 h at 210°C. This  $T_g$  is close to the initial  $T_g$  value of the solution polymerized Ultem® DA-DODA-DAP (5/5) copolyimide (see Fig. 3). Similar glass transition behaviors are also observed in DMA experiments. An emergence of two  $\tan\delta$  relaxation processes can be found as shown in Fig. 5. These results indicate that a random copolyimide may be produced from the homopolyimide mixture after the heat-treatment. A transimidization chemical reaction may thus occur to result in rearrangement of Ultem® DA-DODA and Ultem® DA-DAP units along the polymer chain backbones.

Figure 6 provides evidence for the actual occurrence of the transimidization reaction by monitoring the intrinsic viscosity change in the system during the heat treatment. Note that a viscosity change reflects a change in molecular weight. The intrinsic viscosity of the initial mixture is 0.86 dL/g. Although this value is a combination of both homopolymers, it is closer to the intrinsic viscosity of Ultem® DA-DODA homopolymer (0.94 dL/g) than that of Ultem® DA-DAP homopolymer (0.75 dL/g), since the measurement of intrinsic viscosity is more sensitive to the higher molecular weight side<sup>[20]</sup>. After 2 h of heat-treatment the intrinsic viscosity shows a decrease of about 20% to 0.70 dL/g, and then is followed by a gradual decrease with further increasing the heat-treatment time. These results clearly reveal a change in molecular weight and therefore, a possible occurrence of the transimidization reaction.

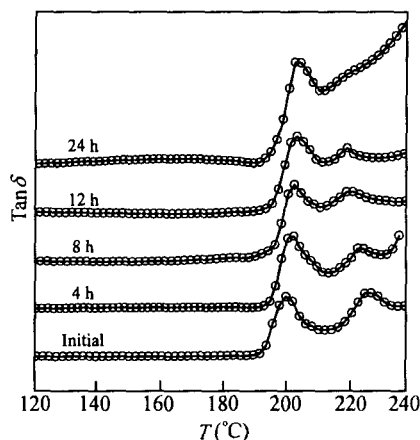


**Fig. 5** Dynamic mechanical behavior of Ultem® DA-DODA/Ultem® DA-DAP mixture with heat-treatment time at 210°C in *p*-chlorophenol

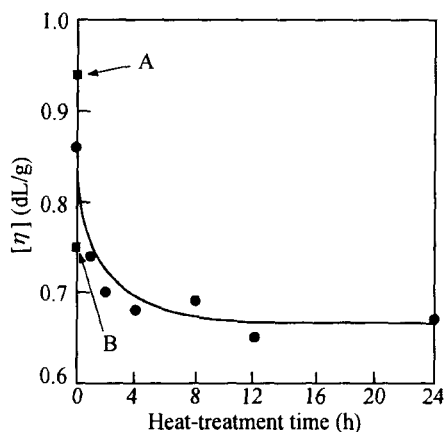


**Fig. 6** Intrinsic viscosity of Ultem® DA-DODA/Ultem® DA-DAP mixture with heat-treatment time at 210°C in *p*-chlorophenol

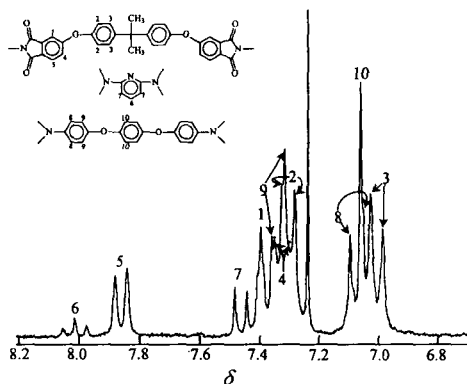


**Fig. 7** <sup>1</sup>H-NMR spectrum of Ultem® DA-DODA-DAP (5/5) copolymer with peak assignments

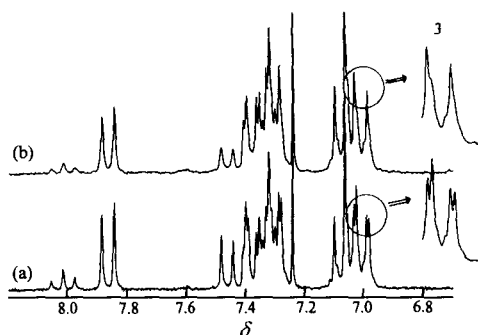


**Fig. 8** <sup>1</sup>H-NMR spectra of Ultem® DA-DODA/Ultem® DA-DAP mixture (a) before and (b) after heat treatment at 210°C in *p*-chlorophenol for 24 h [0.5% (g/cm<sup>3</sup>) in CDCl<sub>3</sub>]

Direct proof of the transimidization can be found by the analysis of chain structure using solution NMR experiments. Figure 7 shows a <sup>1</sup>H-NMR spectrum of Ultem® DA-DODA-DAP (5/5) copolymer [0.5% (g/cm<sup>3</sup>) in CDCl<sub>3</sub>], where peak assignments have been confirmed by a 2D-COSY technique<sup>[17-19]</sup>. Figure 8 contains <sup>1</sup>H-NMR spectra of the mixture in initial and final states. Note that two *T<sub>g</sub>*s are found in the initial state while only one *T<sub>g</sub>* is observed in the final state. When the

spectrum of the final state is compared to that of the NMR spectrum of the copolyimide in Fig. 7, they are virtually identical in the peak positions of chemical shifts. On the other hand, when one compares the spectra between the initial and final states, the proton resonance corresponding to Ultem® DA units in the final state appear to be broader than those in the spectrum of the initial state. For example, the No. 3 proton resonance of the final state exhibits a broader doublet while the initial mixture shows a resonance consisting of two distinct doublets: one doublet is from DODA-Ultem® DA-DODA segments and the other is from DAP-Ultem® DA-DAP segments. During the heat-treatment, transimidization occurs in rearranging these two repeating units along the chain backbones. As a result, the final state becomes a copolyimide that has a more or less random distribution of the Ultem® DA-DODA and Ultem® DA-DAP repeating units, similar to the case of Ultem® DA-DODA-DAP (5/5).

Figures 9 and 10 show  $^1\text{H-NMR}$  spectra (on a 300 MHz NMR) at a higher concentration of about 2% ( $\text{g}/\text{cm}^3$ ) for the mixture after the heat-treatment. In addition to the previous observations of the broadened doublet, chemical shifts with a weak intensity appear at around 6.6, which can be clearly seen in Fig. 10 for the mixture after heat treatment of 24 h. It is speculated that these chemical shifts may be related to the protons in the chain end groups. The control of stoichiometry enables us to prepare two kinds of oligomers derived from Ultem® DA and DODA: one has Ultem® DA end-capped and the other has DODA end-capped oligomers. The comparison between their  $^1\text{H-NMR}$  spectra, as shown in Fig. 11, indicates that the chemical shift of the aromatic protons in DODA end groups is at about 6.9. The same approach can also be used for the oligomers derived from Ultem® DA and DAP, and their spectra are shown in Fig. 12. At around 6.6 the chemical shift is attributed to the protons of DAP end groups which show two doublet resonances. Therefore, most of the chains in the mixture after the heat treatment of 24 h are DAP end-capped. This is achieved through the transimidization process.

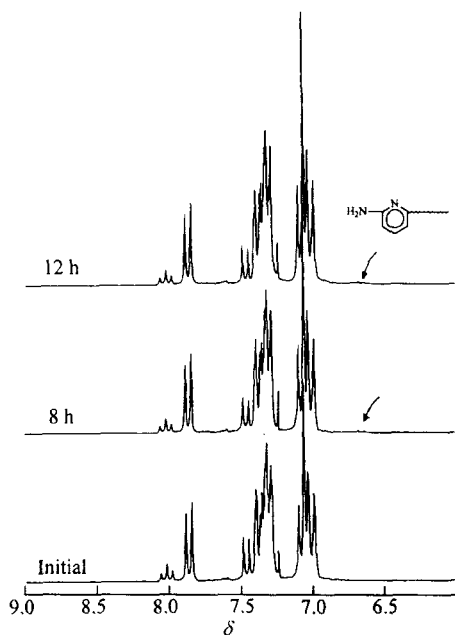


**Fig. 9**  $^1\text{H-NMR}$  spectra of Ultem® DA-DODA/ Ultem® DA-DAP mixture after heat-treated at  $210^\circ\text{C}$  in *p*-chlorophenol for various times [ $\sim 2\%$  ( $\text{g}/\text{cm}^3$ ) in  $\text{CDCl}_3$ ]

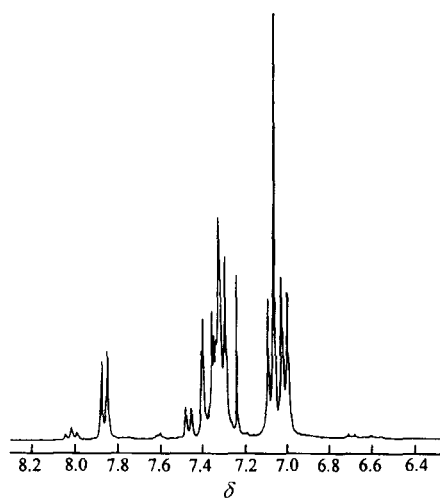


**Fig. 10**  $^1\text{H-NMR}$  spectra of Ultem® DA-DODA/ Ultem® DA-DAP mixture after heat treatment at  $210^\circ\text{C}$  in *p*-chlorophenol for 24 h (300 MHz;  $\sim 2\%$  ( $\text{g}/\text{cm}^3$ ) in  $\text{CDCl}_3$ )

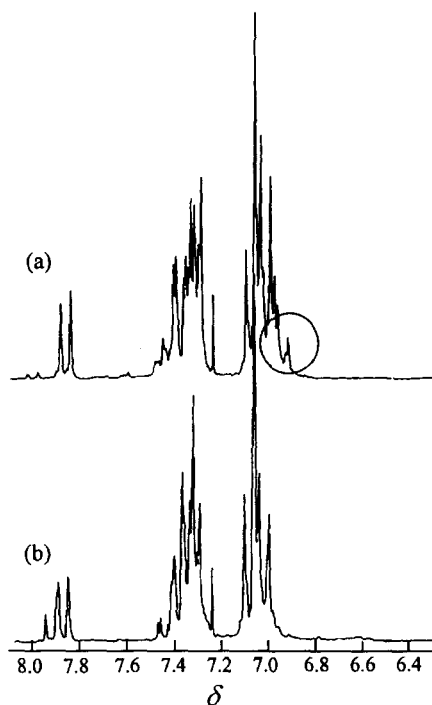


**Fig. 11**  $^1\text{H}$ -NMR spectra of Ultem<sup>®</sup> DA-DODA oligomers obtained from the monomer feed ratios of Ultem<sup>®</sup> DA:DODA= (a) 0.75:1 and (b) 1:0.5

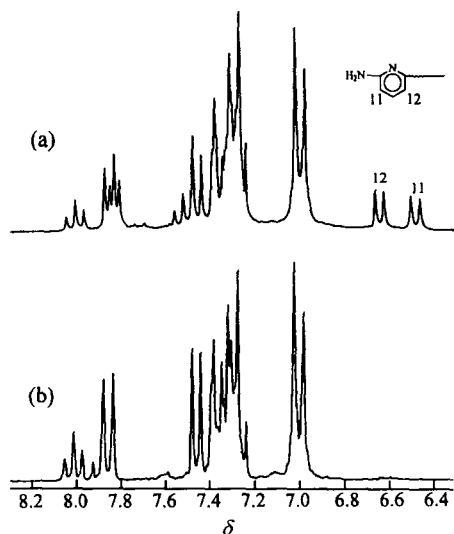


**Fig. 12**  $^1\text{H}$ -NMR spectra of Ultem<sup>®</sup> DA-DAP oligomers obtained from the monomer feed ratios of Ultem<sup>®</sup> DA:DAP= (a) 0.5:1 and (b) 1:0.8

Since all the protons in DODA units show resonance which are overlapped with aromatic protons in Ultem<sup>®</sup> DA units between 7.0 and 7.4, it is very difficult to obtain a quantitative result from the peak area integration. Figure 13 presents a  $^{13}\text{C}$ -NMR spectrum of Ultem<sup>®</sup> DA-DODA-DAP (5/5) copolymer with the peak assignments. Also,  $^{13}\text{C}$  resonance from DAP end-capped copolyimide are identified using two types of oligomers derived from Ultem<sup>®</sup> DA and DAP with

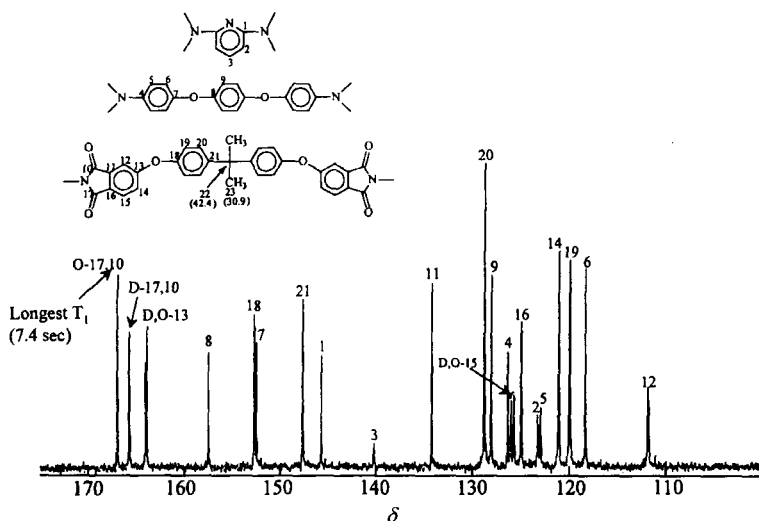


**Fig. 13**  $^{13}\text{C}$ -NMR spectrum of Ultem<sup>®</sup> DA-DODA-DAP (5/5) copolyimide with peak assignments

different end-capped groups, as depicted in Fig. 14. With a proper parameter set for completion of spin relaxation and elimination of NOESY,  $^{13}\text{C}$ -NMR spectra were recorded for the initial mixture and the final state (Fig. 15). Unlike the  $^1\text{H}$ -NMR spectra, the  $^{13}\text{C}$ -NMR spectral width is too broad to show delicate differences. Yet, the peak area integration with an unavoidable experimental error of 5% gives us the mol% ratio of diamines incorporated into the chain backbones. The average mol% ratios of DODA to DAP are 54% to 46% for the initial mixture and 62% to 38% for the final state. This indicates that the transimidization causes approximately 15% of DAP initially located within the chain backbones either to be moved to the chain ends or even to be liberated back to monomers which may be washed out during the polymer precipitation process in methanol.

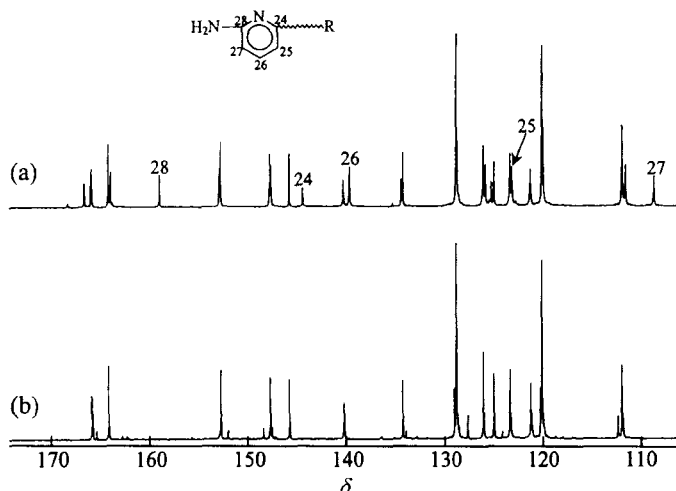


**Fig. 14**  $^{13}\text{C}$ -NMR spectra of Ultem<sup>®</sup> DA-DAP oligomers obtained from the monomer feed ratios of Ultem<sup>®</sup> DA:DAP= (a) 0.5:1 and (b) 1:0.8

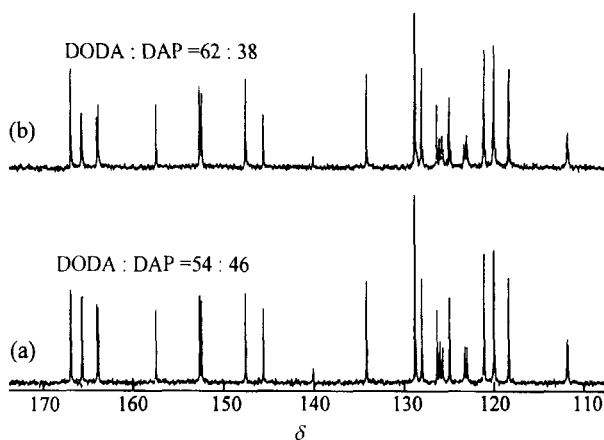


**Fig. 15**  $^{13}\text{C}$ -NMR spectra ( $D_1=5 \times T_1$  &  $\text{DM}=\text{NNY}$ ) of Ultem<sup>®</sup> DA-DODA/Ultem<sup>®</sup> DA-DAP mixture (a) before and (b) after heat treatment at 210°C in p-chlorophenol for 24 h

The search for more evidence for the transimidization in the polyimide mixture system was also been attempted using the 2D-NOESY technique, of which NOE of superficially closed protons (within approximately 0.5 nm distance) can be detected as a cross peak in chemical shift. The idea

comes from the result that in the initial phase-separated mixture (showing two  $T_g$ s) the average distance between the protons in DODA and DAP units in two different polymers must far exceed the 0.5 nm distance range. However, for the final copolyimide having only one  $T_g$ , there might be a greater possibility for the average distance to be within the 0.5 nm range. If this were true, the cross peaks should appear in a 2D-NOESY spectrum due to dipole-dipole interactions between specifically closed DODA and DAP units within a copolyimide chain backbone. Figure 16 presents 2D-NOESY spectra of the initial mixture and the final copolyimide having 0.5% (g/cm<sup>3</sup>) concentrations. Contrary to expectations, neither spectra in Fig. 16 show any cross peaks between the DODA and DAP units, nor do the spectra of Ultem® DA-DODA-DAP (5/5) copolymer with the same concentration, as shown in Fig. 17. The only cross peaks are attributed to the interactions between the Ultem® DA units with either the DODA or DAP units. A higher sample concentration of 10% (g/cm<sup>3</sup>) has also been used for Ultem® DA-DODA-DAP (5/5) copolymer, and it gives an uninterpretable spectrum. Failure of the expected observation may be explained *via* an electronic polarization (or even possibly, a charge-transfer) mechanism proposed for the chain-chain interaction in a linear aromatic polyimide<sup>[2]</sup>. This electronic polarization type of interaction should be viewed as a Lewis acid-base interaction (electron donor-electron acceptor), which is more likely to form between an electron-deficient dianhydride and an electron-rich diamine-derived

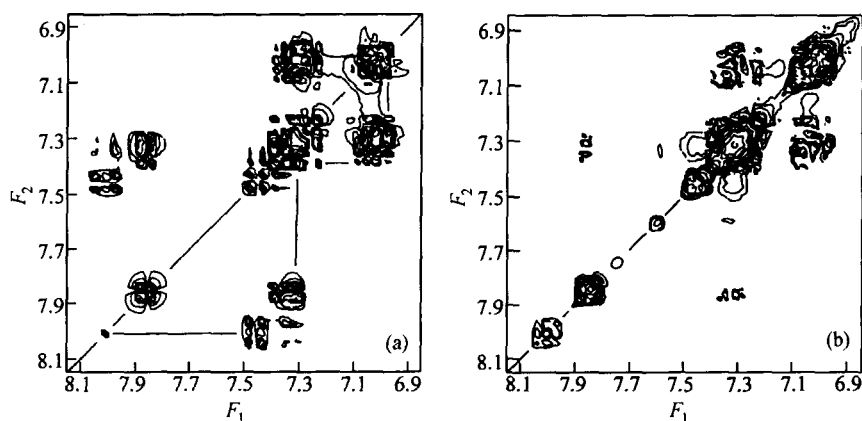


Fig. 16 <sup>1</sup>H-NOESY spectra of Ultem® DA-DODA/Ultem® DA-DAP mixture (a) before and (b) after heat treatment at 210°C in *p*-chlorophenol for 24 h [0.5% (g/cm<sup>3</sup>) in CDCl<sub>3</sub>]

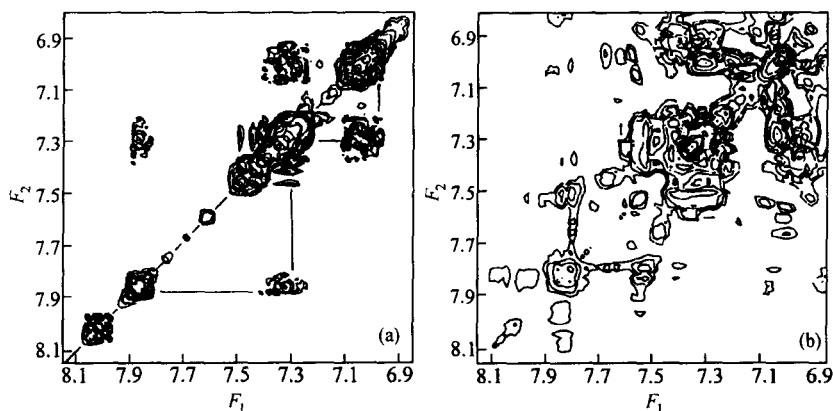


Fig. 17 <sup>1</sup>H-NOESY spectra of Ultem® DA-DODA-DAP (5/5) copolyimide with concentrations of (a) 0.5% and (b) 10% (g/cm<sup>3</sup>) in CDCl<sub>3</sub>

moieties. This explanation may result in the possible observation of cross peaks between Ultem® DA units with either the DODA or DAP units, which has been experimentally found. On the hypothesis that the intensity of a cross peak has relations with the strength of electronic interactions, the comparison of both spectra in Fig. 16 shows that such electronic interactions between chains in the mixture decrease after the heat-treatment. Namely, each homopolyimide in the initial mixture showing its own interactions between the dianhydrides and diamines undergoes transimidization, and the final copolyimide has fewer chain-chain interactions resulting from the incorporation of electron-deficient and kink-like DAP units into Ultem® DA-DODA chain backbones. This can be verified by the methods, which are often applied to lower such interactions in linear aromatic polyimides. These include incorporating kinks in the polyimide backbone using *ortho* or *meta* catenation, introducing electron-withdrawing groups in the diamine and electron-donating groups in the dianhydride, incorporating bulky units along the chain and combinations of these techniques<sup>[2]</sup>. Therefore, it can be seen that the 2-D NOESY spectra in Fig. 16 provide more supporting evidence of transimidization in the homopolyimide mixture.

On the other hand, transimidization has been studied in the melt of Ultem® DA-DODA and Ultem® DA-DAP mixture. The initial mixture was also heat-treated in melt state at 310°C, about 80°C above the higher  $T_g$  under nitrogen atmosphere for a predetermined time. As shown in Fig. 18, a similar glass transition behavior to the solution heat-treated mixture (Fig. 4) is observed, and the final product after 23 h heat-treatment is an Ultem® DA-DODA-DAP random copolyimide having one  $T_g$  and still soluble in *p*-chlorophenol. The final  $T_g$  at 227°C is about 15°C higher than that of the final product from solution heat-treatment. This result indicates that the released DAP units are reactive at the high temperature, and they re-incorporate into the copolymer chains *via* transimidization. As a result, molecules may undergo chain extension and more DAP units are incorporated in the chains than are obtained by the copolyimide in the final state of heat-treated solution system.

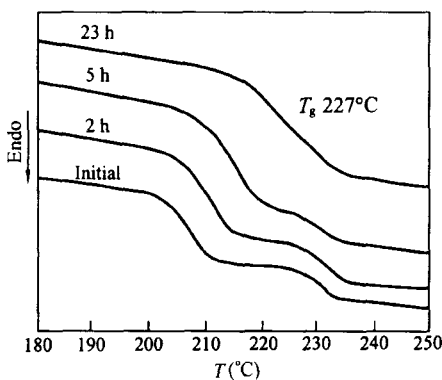


Fig. 18 DSC thermograms of Ultem® DA-DODA/Ultem® DA-DAP mixture before and after heat treatment at 310°C in the melt state under dried N<sub>2</sub> for various times

#### **Transimidization in Ultem® DA-DODA/DAP and Ultem® DA-DAP/DODA Mixture in *p*-Chlorophenol**

Up to this point, we have provided experimental evidence of transimidization in the mixture of homopolyimides. The remaining question is how transimidization proceeds in the homopolyimide mixture. This can be deduced from the study of transimidization on a homopolyimide by an added nucleophile. First, Ultem® DA-DODA homopolymer was heat-treated in DAP/*p*-chlorophenol solution at 210°C for 12 h. The resulting polymers were then precipitated in methanol in order to study a change of the chain structure resulting from the transimidization. If the transimidization

takes place, the DAP monomers must attack Ultem® DA-DODA units. The  $^1\text{H-NMR}$  spectrum of the resulting polymer after heat-treatment is almost the same as that of the Ultem® DA-DODA homopolyimide (Fig. 19) except for the weak intensities of the chemical shift peaks at around 6.6. The earlier study on Ultem® DA-DAP oligomers has already revealed that these peaks are the resonances of aromatic protons in DAP end-capped units. The peaks at about 6.9 corresponding to the DODA end-capped units still remain in the  $^1\text{H-NMR}$  spectrum of the resulting polymer after the heat treatment. Solution viscosity measurements yield an intrinsic viscosity of 0.8 dL/g for the resulting polymer, whereas 0.9 dL/g for the initial Ultem® DA-DODA homopolymer. These results indicate that under such a heat-treatment DAP monomers may attack Ultem® DA-DODA imide linkages. Nevertheless, the transimidization is not effective. This can be supported by the viscosity measurements (0.9 dL/g *versus* 0.8 dL/g) since the transimidization caused by DAP monomers should result in the chain scission. It is possible for a DAP monomer to react with an Ultem® DA unit at the end of a chain without undergoing a chain extension. This may be seen by the absence of a triplet resonance at 8.02 from the No.6 proton (see Fig. 7) which represents the resonance of DAP units incorporated in the chain backbones.

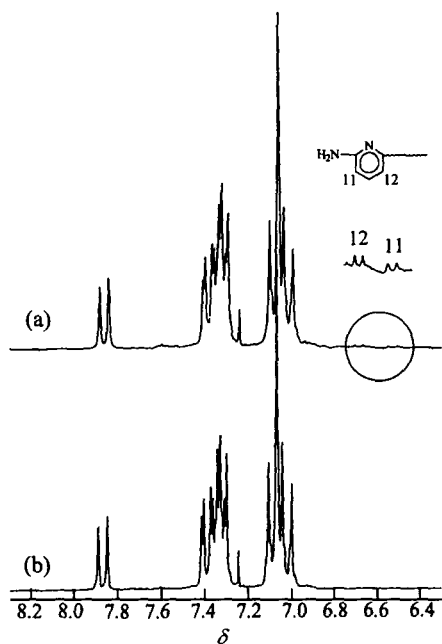


**Fig. 19**  $^1\text{H-NMR}$  spectra of Ultem® DA-DODA homopolyimide (a) before and (b) after heat treatment at 210°C for 12 h in DAP/*p*-chlorophenol

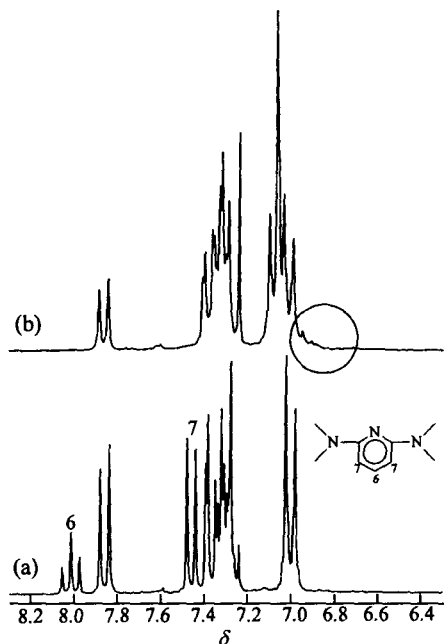


**Fig. 20**  $^1\text{H-NMR}$  spectra of Ultem® DA-DAP homopolyimide (a) before and (b) after heat treatment at 210°C for 12 h in DODA/*p*-chlorophenol

After the Ultem® DA-DAP homopolymer was heat-treated in DODA/*p*-chlorophenol solution at 210°C for 12 h, the  $^1\text{H-NMR}$  spectrum shows that, unlike the previous observation, all the proton resonance from DAP units disappear (Fig. 20). The peaks at about 6.9, attributed to the DODA end-units, also appear in the  $^1\text{H-NMR}$  spectrum of the resulting polymer. This spectrum turns out to be identical to the  $^1\text{H-NMR}$  spectrum of Ultem® DA-DODA homopolymer. The intrinsic viscosity, initially 0.4 dL/g for Ultem® DA-DAP homopolymer (prepared from another batch), is increased to 0.6 dL/g for the resulting polymer. It is evident that all the Ultem® DA-DAP imide linkages are readily attacked and transimidized by DODA monomers accompanied by chain extension, and an Ultem® DA-DODA homopolyimide is virtually produced. The same results were

also observed by  $^{13}\text{C}$ -NMR experiments.

## CONCLUSION

From all the results, the following scheme is proposed to explain what has happened in this homopolyimide mixture system during the heat treatment. Initially, each homopolymer in the mixture contributes to its own glass transition temperature, Ultem<sup>®</sup> DA-DODA homopolymer to  $T_{g1}$  and Ultem<sup>®</sup> DA-DAP homopolymer to  $T_{g2}$ . Since Ultem<sup>®</sup> DA-DAP imide linkages are very susceptible to the transimidization by DODA-ended groups, Ultem<sup>®</sup> DA-DODA homopolymer chain ends readily attack the Ultem<sup>®</sup> DA-DAP homopolymer chains to decrease the chain length of this polymer during the heat treatment. A new Ultem<sup>®</sup> DA-DODA-DAP block copolymer forms in the early stage of transimidization. However, the transimidization by DODA-ended chains also produces a higher population of DAP-end capped chains, giving DAP-ended chains more chances to transimidize back onto Ultem<sup>®</sup> DA-DODA imide linkages. This resulting copolymer with a decreased molecular weight, compared to the Ultem<sup>®</sup> DA-DODA-DAP block copolymer formed at the early stage, contributes to  $T_{g1}$ , while the remaining chain-scissioned Ultem<sup>®</sup> DA-DAP homopolymer contributes to  $T_{g2}$ . As further transimidization goes on, the shorter Ultem<sup>®</sup> DA-DAP segments contribute to  $T_{g2}$ . Finally, after around 24 h of transimidization occurring, a random Ultem<sup>®</sup> DA-DODA-DAP copolymer having only one  $T_g$  is produced with the mol% ratio of DODA to DAP being 62% to 38%. Approximately 15% of DAP units, initially incorporated in the chains, are pushed out of the chains either to locate at the chain ends to result in the higher population of DAP-ends than DODA-ends, or are washed out during the polymer precipitation process. A similar mechanism may also be proposed for the transimidization in the molten state.

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