Synthesis of Poly(*p*-phenyleneterephthalamide) by Solid-Phase Polymerization

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ABSTRACT: Poly(*p*-phenyleneterephthalamide) (PPTA) chain extension reactions, notably the catalyzed condensation of diphenyl terephthalate with *p*-phenylenediamine, are severely limited, at reaction temperatures up to at least 400 °C, by immobilization of the growing macromolecules at modest molecular weight (MW) levels. This is characteristic of the stiff, extended nature of the polymer chains and their high propensity to crystallize. However, the phenolysis reaction can proceed very rapidly above a threshold temperature of about 475 °C such that very high MW (η_{inh} = 5–9 dL/g in H_2SO_4) is achievable by brief heating at about 530 °C. Novel techniques have been devised to subject the material to be polymerized (a monomer–catalyst mixture or a low-MW oligomer) to high temperatures for a very short time. The threshold temperature is believed to signal the level beyond which the PPTA chains develop considerable segmental mobility such that interchange of amino ends with adjacent amide groups can occur freely. Ultimately an amino end will interchange with a phenyl ester group to liberate phenol which can diffuse out of the system for a net gain of one amide group. The effects of catalysts, byproduct elimination rate, and heat-up rate are considered. In all cases polymerization was accompanied by some branching which, while not detectable by most conventional analytical procedures, caused major adverse changes in the viscosity and shear sensitivity of sulfuric acid solutions. A consideration of model compound reactions attributed branching to disproportionation of two amide groups to form an amidine branch point.

Introduction

Compared with most other aramids, poly(*p*-phenyleneterephthalamide) (PPTA) has relatively inflexible, extended polymer chains. Its high persistence length of 25 nm[1] is roughly one-quarter the length of high-MW PPTA macromolecules used in the manufacture of Kevlar aramid fibers. In contrast, the much more flexible, nonextended, isomeric poly(*m*-phenyleneisophthalamide) (MPIA) has a persistence length of only 2.0 nm.[2] A consequence of this characteristic of PPTA, of immense practical importance, is the transition to a liquid crystalline phase above some limiting solution concentration. The macromolecules are in this way fully extended, and when subjected to shearing and extensional forces, as in fiber spinning, they develop a high degree of molecular alignment, which is captured by subsequent coagulation in a nonsolvent and is the basis of high fiber strength and modulus. The same characteristic is also responsible for the relative intractability of PPTA in terms of insolubility in organic solvents and the very high melting temperature, which is well above the temperature (500 °C) of incipient pyrolytic weight loss. Because of its limited flexibility, the gain in entropy on melting is quite small (estimated heat of fusion[3] is only 13.1 kJ/mol), so that hypothetical melting points are well above 500 °C. DSC suggests a melting temperature of 560 °C[4] whereas the extrapolated melting points of a series of well-defined oligomers indicate 718 °C.[3] The inherent low mobility of the PPTA chains is reinforced by a strong propensity toward macromolecular alignment and crystallization and a capacity for hydrogen bonding between amide groups. The much more flexible MPIA melts a good deal lower, at about 410 °C; its glass transition temperature is 265 °C, versus about 400 °C for PPTA. In addition, MPIA dissolves in a variety of organic and acid solvents, whereas PPTA is soluble only in a few strong acids.

For the formation of PPTA by the commonly used low-temperature solution polymerization,[5] the combination of terephthaloyl chloride with *p*-phenylenediamine (PPD) in most organic solvents gives a low-MW product because the process is terminated by precipitation at an early stage ($\eta_{inh} \sim 1.0$ dL/g; $\bar{M}_n \sim 5000$). Fortunately, a few solvent systems allow the formation of an appreciably higher MW before fluidity is lost, and in their eventual gel state there is sufficient motion of the macromolecules to allow continued combination of reactive ends and growth to high MW (a high level of fiber strength and toughness requires $\bar{M}_n$ of at least 21 000, corresponding to η_{inh} of at least 5 dL/g in sulfuric acid[2]). Best known of these solvents are *N*-methylpyrrolidone (NMP)/hexamethylphosphoramide (2:1),[6] hexamethylphosphoramide,[7] and NMP/$CaCl_2$.[8] For spinning, casting, or other shaping processes the polymer must be isolated by precipitation with water and subsequently redissolved in 100% sulfuric acid. A two-solvent procedure is obviously less convenient and desirable than the use of a single organic solvent as is possible for more soluble, flexible polymers. For MPIA, for example, the polymerizate in dimethylacetamide may be converted directly into a spinnable dope by neutralization of the HCl byproduct with added CaO to form solubility-enhancing $CaCl_2$ in situ.

Alternative methods of forming high-MW PPTA, avoiding the use of two solvents, have attracted appreciable attention. Attempts to utilize sulfuric acid, the spinning solvent of choice, which can dissolve up to 20% by weight of PPTA, as polymerization medium were unsuccessful.[9] Slightly higher MW polymer (η_{inh} = 1.6 dL/g) was obtained in liquid SO_3[10] (which may be converted to H_2SO_4 by addition of water), but the product was significantly sulfonated. A novel approach was elimination of a solvent altogether by combining terephthaloyl chloride and PPD in the vapor state,[11] but the higher MW products were invariably branched to an extent that caused sulfuric acid solutions to be excessively viscous.

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Certain low-melting, amorphous aramid copolymers have been polymerized to high MW in the absence of a solvent at elevated temperatures by catalyzed condensation of dicarboxylic acids with diacetamides[12] or of diphenyl esters with diamines.[13] The acetolysis reaction has been exploited in the preparation of liquid crystalline melt poly(ester–amides) as both a melt and a solid-state process.[14] Solid-state polymerization has long been used as a route to especially high-MW nylons or polyesters but has not been successful for high-melting, crystalline aramids. For example, low-MW polymer only was the result when *m*-phenylenediamine and diphenyl isophthalate,[2] phenyl-*p*-aminobenzoate,[15] or *p*-acetamidobenzoic acid[16] were heated at temperatures up to 400 °C. [An unusual reaction was the preparation of high molecular weight (inherent viscosities up to 4.8 dL/g) poly(*p*-benzamide) via solid-state polymerization at 400 °C of the adduct from *p*-aminobenzoic acid and carbon disulfide in nitrobenzene.[17]] Likewise, low-MW polymer of η_{inh} = 1–2 dL/g was formed by the reaction of terephthalic acid with PPD at 375 °C during several hours in the presence of catalysts (boric acid, *p*-toluenesulfonic acid, or tetraphenyltin).[2,15] Use of dimethyl or diisopropyl esters of terephthalic acid, rather than the acid itself, gave no significant improvement,[2] but diphenyl terephthalate (DPT) gave polymer with η_{inh} of 3.3 dL/g or higher.[2,9] Frazer[9] noted that the latter reaction could be accelerated by a variety of catalysts at temperatures below 400 °C but polymerization was always accompanied by some degree of chain branching. Reactions of terephthalic acid with diacetylated PPD in the same temperature range yielded low-MW product; this might be largely the result of decarboxylation, which occurs at a significant rate above about 350 °C.

The catalyzed condensation of a phenyl ester with an aromatic amine may proceed in high yield at 300 °C or lower, if byproduct phenol is continuously removed from the system. However, the limitation of the DPT–PPD reaction to modest levels of MW in the PPTA product at temperatures up to at least 400 °C, as observed in preceding work, suggests that the polymerization is slowed down and terminated by some competing process. A reasonable hypothesis is that the relatively inflexible PPTA macromolecules become less and less mobile as they increase in length so that reactive chain ends find it increasingly difficult to find each other and condense, and eventually chain growth stops. Immobilization of chain ends would be accentuated by the propensity of PPTA to crystallize and form intermolecular hydrogen bonds. Both MW growth to some limiting level and immobilization of PPTA chains appear to be fairly rapid processes. The apparent slow continued increase in inherent viscosity levels, with prolonged heating in the ca. 400 °C range reflects chain branching processes that are not completely suppressed by immobilization of PPTA chains. Branching at quite low levels can exert a profound effect on solution viscosities.

Experimental Section

Materials. Diphenyl terephthalate (DPT) was crystallized from xylene to give a cryoscopic freezing point of 197.6 °C.

***p*-Phenylenediamine** (PPD), from Du Pont, had fp 140.8 °C.

PPTA prepolymer, η_{inh} = 0.12–0.15 dL/g in sulfuric acid, was prepared by heating a stoichiometric mixture of PPD and DPT until equilibrium phenol reflux conditions were attained. Higher MW prepolymer was obtained by distilling off a portion of the byproduct phenol and reestablishing equilibrium reflux.

4′-Amino-4-carbophenoxybenzanilide[8] was prepared by condensation of phenol with 4-carboxybenzoyl chloride, conversion with thionyl chloride to 4-carbophenoxybenzoyl chloride, condensation with 4-nitroaniline, and hydrogenation of the formed 4′-nitro-4-carbophenoxybenzanilide.

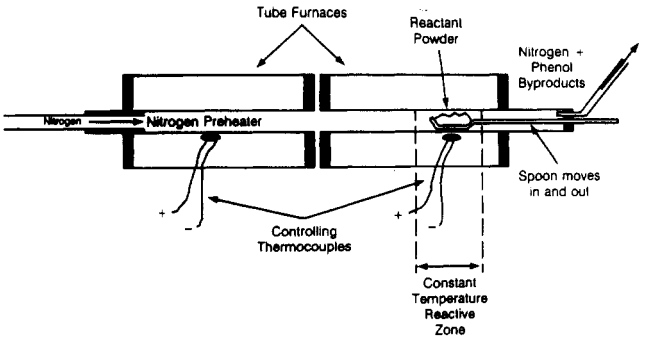


Figure 1. Tube furnace technique. The reaction zone is preheated to the desired reaction temperature as measured on the inner surface of the quartz tube. The spoon carrying the reactant powders is moved into the reaction zone and semirotated to deposit the reactants onto the hot tube surface. The tube is simultaneously rotated to spread reactants as a thin layer or film. Reaction is terminated by opening the furnace and cooling the tube in a blast of cold air.

Terephthalanilide was formed as a pure precipitate by reaction of terephthaloyl chloride with the stoichiometric amount of aniline in dimethylacetamide.

***p*-Phenylenedibenzamide** was likewise formed from PPD and benzoyl chloride.

Polymerization Techniques. (1) Tube Furnace (Figure 1). A slow current of nitrogen, to exclude air, enters a quartz tube, which passes through two side-by-side tube furnaces in series. The first of these serves to preheat the nitrogen. The second contains the constant-temperature reaction zone as determined by a removable thermocouple in contact with the tube's inner surface. Through a stopper at the exit end of the tube is an outlet for the nitrogen and entrained polymerization byproduct, phenol, and a close-fitting, lubricated glass rod that may be pushed in or out through a second hole. When the reaction zone has attained the desired temperature, the material to be polymerized (about 0.2 g), contained in a spoon attached to the end of the glass rod, is moved into the reaction zone and dropped onto the inner surface of the quartz tube. A brief rotary motion of the tube causes it to spread as a thin layer. At the end of the desired reaction period, the furnaces are quickly opened, and the tube, with nitrogen still flowing within, is cooled in an external blast of cold air. The polymerization may also be operated in a reduced pressure of a few torrs by bleeding in nitrogen slowly and attaching the gas exit tube to a vacuum pump. The volatile byproducts of the polymerization under ambient or reduced pressure may be collected for analysis in a cold trap. Polymerization may be conducted in the presence of HCl by admixing the desired proportion of HCl with the entering nitrogen stream. The material to be polymerized may be a low-MW, involatile, powdered PPTA prepolymer or a powdered mixture of monomers and catalyst briefly premelted to ensure intimate mixing.

(2) Steel Belt (Figure 2). A nitrogen-blanketed, motor-driven steel belt passes through a reaction zone in which the belt surface is maintained at a desired temperature by contact with heating plates mounted underneath and noncontact radiant heaters above. Finely divided prepolymer or, alternatively, monomer–catalyst mixture is deposited by a suitable vibrating feeding device via a 5-cm-wide slot as a thin layer on the upper surface of the preheated belt. Subsequent high-temperature exposure is determined by variation in the belt speed. Byproduct phenol is swept away in the nitrogen stream and condensed. Polymeric product is scraped off the belt at the end of the heating zone into a catch pot. With this apparatus high thermal expansion of the belt at reaction temperatures posed certain practical difficulties.

(3) Fluidized Bed. PPTA prepolymer is compacted into coherent thin disks (1.0 g; 3-cm diameter × 0.3 cm thick) in a die or pelletizing machine at 20 000 psi. These are contained in wire mesh cages that can be immersed for the desired reaction time in a standard laboratory heating bath of an Alundum bed (15 kg) fluidized with heated nitrogen at 4 psi. Byproduct phenol is removed immediately in the upflow of nitrogen. The disks maintain their integrity through conversion to high polymer. The prepolymer must have η_{inh} of at least 0.3 dL/g to eliminate

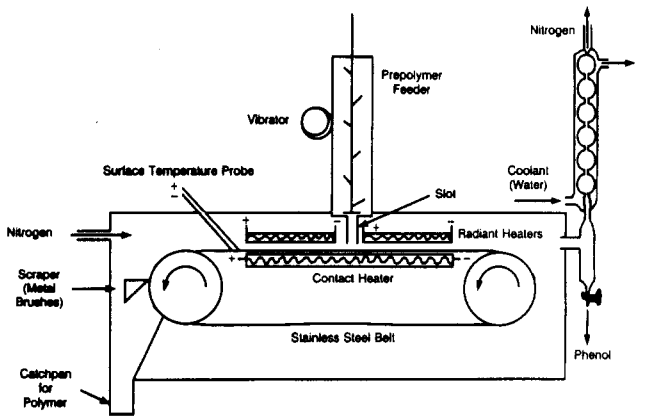


Figure 2. Continuous belt polymerizer. Prepolymer or monomer–catalyst mixture is metered via a 2-in.-wide slot as a thin layer or film on a steel belt moving over a control heater and underneath a radiant heater. Temperature and time are precisely controlled. Product scraped off the belt collects in a catch pot.

sticking of Alundum particles to the disk surface. This technique allows larger amounts of polymer to be prepared in a convenient way than is possible via the tube furnace. The large heat capacity of the bath avoids local cooling, and temperature is accurately controllable, e.g., to ±2 °C at 500 °C.

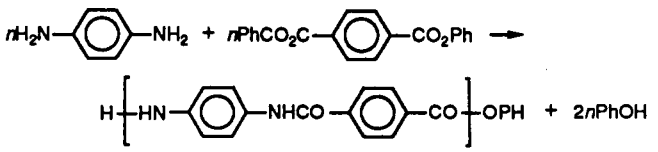
Characterization of Polymer via Methanolysis. To detect possible branch points PPTA polymers were degraded back to subunits that could be quantitatively analyzed. Polymer (1.00 g), methanol (1.2 g), and HF (20 g) were heated together in a Hastelloy C rocker tube for 5 h at 100 °C. After cooling to room temperature, excess HF was removed by purging with a nitrogen stream, and the residue was extracted four times with 5 parts of chloroform at room temperature by treatment in a Waring blender. The separated chloroform extracts were combined and evaporated to dryness. Methanol solutions of the residue were analyzed by gas chromatography. Dimethyl terephthalate and a minor amount of methyl benzoate (the origin of which is discussed later) was identified.

The residue from the chloroform extraction was dissolved in aqueous Na_2CO_3, the resulting solution extracted with ether, the ether extract dried over Na_2SO_4 and then evaporated to dryness. Thin-layer chromatography on a silica gel GF/250 mm plate utilized chloroform/methanol (65/35 vol %) as the spotting solvent and a 95/5 vol % mixture of the same as eluent. Fluorescent fractions were detected under an ultraviolet light. PPD was also readily visible as a dark spot resulting from partial oxidation in air. The chromatograms of our PPTA products showed basically PPD together with a number of unidentified fluorescent materials present in minute amounts. The latter were absent in the methanolysate of linear PPTA as used for manufacture of Kevlar aramid fiber.

Fabrication of Flexible Films. Solutions (5% (w/w)) of high-temperature PPTA in 100% H_2SO_4 were placed on a clear glass plate, using a doctor's knife, as a film. This was coagulated with water, washed free of acid, and dried at 80 °C. The flexible nature of the film qualitatively evidenced the comparatively high MW, linear nature of the polymer.

Results

Earlier work suggested that the best prospects for preparing PPTA in high MW by a nonsolvent route is the condensation of DPT with PPD, if conditions could be



found whereby phenolysis polymerization would far outpace MW-limiting processes, as well as undesirable side reactions, notably chain branching and pyrolytic decomposition. This would require temperatures higher than those used previously, efficient removal of byproduct phenol, and perhaps a potent catalyst. The upper limit of temperature would probably be in the range 500–560 °C, where pyrolysis becomes increasingly rapid. To avoid branching reactions, which are not completely suppressed at lower temperatures, the material to be polymerized would have to be heated extremely rapidly to some well-controlled ceiling temperature, where it would be held for a precise, brief length of time and then rapidly cooled. To facilitate elimination of byproduct phenol, the substrate would be reacted as thin layers in which diffusion distances are small. As with other polyamidation processes, it would be expected that maintenance of an exact stoichiometric ratio of reactive end groups throughout the course of the polymerization would be important.

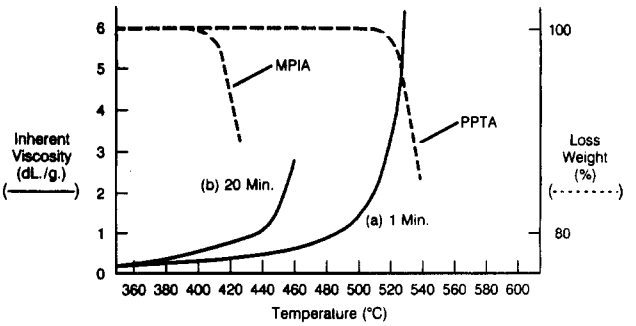


Figure 3. Effect on inherent viscosity (in sulfuric acid) of heating PPTA prepolymer for (a) 1.0 min and (b) 20 min at a series of increasing temperatures (solid curves). Weight loss in nitrogen by TGA for PPTA and MPIA.

Novel polymerization techniques were devised to provide high reaction temperatures and very fast heating and cooling rates. In the tube furnace method a PPTA prepolymer is contacted for a specific time with the preheated inner surface of a quartz tube. Most data in this paper are derived from the tube furnace method. In the steel belt method larger amounts of polymer are formed when a thin layer of prepolymer, deposited on a heated moving belt, moves through a heating zone at an adjustable rate. In both these methods a mixture of monomers and catalyst may be used instead of prepolymer but there is some difficulty resulting from adhesion of polymer to the heated reaction surface. In the fluidized bed procedure, also suitable for preparing larger amounts of polymer than the tube furnace method, thin, pressed disks of prepolymer are immersed for a given time in an Alundum bed fluidized by heated nitrogen.

Initial tests confirmed that high-MW PPTA, as measured in terms of inherent viscosity, was formed when prepolymer was heated to 500 °C or above for a short time. When PPTA prepolymer specimens of $\eta_{inh} = 0.15$ dL/g were heated for exactly 1.0 min at a series of increasing temperatures, up to about 500 °C inherent viscosity values did not exceed 1.0 dL/g and were for the most part considerably lower (Figure 3). Much higher values, e.g., 7.5 dL/g at 530 °C, were obtained at temperatures above about 500 °C (Figure 3). There is no correlation between the temperature threshold above which MW dramatically increases and the PPTA glass transition temperature of about 400 °C, but this is not surprising since the latter property pertains to amorphous regions and PPTA has an unusually low content of such regions, being highly crystalline or having a very high degree of macromolecular alignment. It is significant, however, as discussed later, that pyrolytic weight loss in an inert atmosphere, as measured by thermal gravimetric

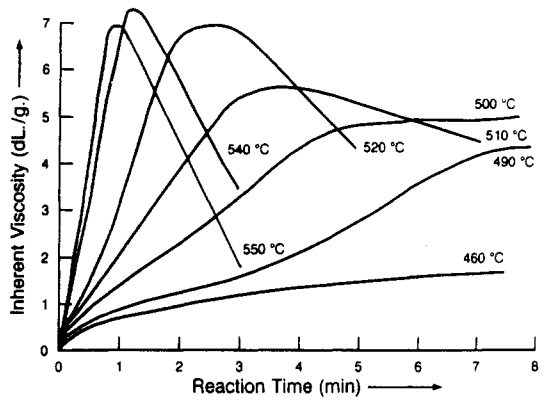


Figure 4. Relationship of inherent viscosity to reaction time at various temperatures for two-stage, uncatalyzed PPTA polymerizations using the tube furnace technique.

analysis, becomes apparent also at about 500 °C for PPTA and proceeds at a fast rate at temperatures beyond this (Figure 3).

When prepolymer specimens were heated for 20 min rather than 1.0 min at a series of increasing temperatures, the threshold temperature for a marked increase in inherent viscosity of the product was about 450 °C; inherent viscosity increased from 1.0 to about 3.0 in the interval 440–460 °C (Figure 3). However, the increase cannot be attributed to normal MW growth but rather to the chain branching. The polymeric product had a brown, as distinct from yellow, color, which was correlatable with PPTA branching. These products were also incompletely soluble in sulfuric acid as is characteristic of cross-linked polymer.

In a separate series of experiments the effect of heating PPTA prepolymer (η_{inh} = 0.15 dL/g) without a catalyst via the tube furnace technique at a series of temperatures in the range 460–550 °C was followed in terms of inherent viscosity changes (Figure 4). Below 475 °C, after an initial small surge in inherent viscosity, further increases were extremely slow and after many minutes of heating it barely exceeded 1.0 dL/g. In the range 475–550 °C the rate of increase and maximum values of inherent viscosity increased sharply such that values of 5–8 dL/g were provided in heating times as brief as 1–2 min at about 530 °C. With excessive heating times the polymer inherent viscosity dropped off markedly after passing through a maximum. At reaction temperatures above 550 °C inherent viscosity maxima diminished, which is not surprising since pyrolysis of PPTA proceeds at a high rate in this region. The drop-off in inherent viscosity is attributed to an increase in the level of chain branching such that cross-links and attendant partial insolubilization appear. Thus in the routine determination of inherent viscosity in sulfuric acid, the incomplete solubility of weighed polymer specimens means that the actual concentration of dissolved polymer is less than the standard 0.5% concentration, so that apparently low values of inherent viscosity result. On this basis, apparent drop in inherent viscosity is a measure of cross-linking. Indeed, linear, high-MW PPTA when heated at very high temperatures likewise loses solubility such that there is an apparent drop in inherent viscosity.

From the shape of the inherent viscosity growth curves in Figure 4, the rate of increase is approximately constant for a given reaction temperature in the 500–550 °C range. Since the Mark–Houwink constant approaches 1.0 for PPTA, the inherent viscosity may be considered to be approximately proportional to molecular weight. It may therefore be concluded that the rate of molecular weight growth under the conditions for a given temperature of

Table I
Pyrolytic Weight Loss during High-Temperature PPTA Polymerization

polymn temp, °C	rate of wt loss, % per min	time of polymn to max inh visc, min	calcd wt loss during polymn, %
490	0.03	10 ± 2	0.28
500	0.04	8 ± 2	0.35
510	0.08	3.7	0.30
530	0.22	2.0	0.44
540	0.24	1.2	0.29
550	0.27	1.0	0.27

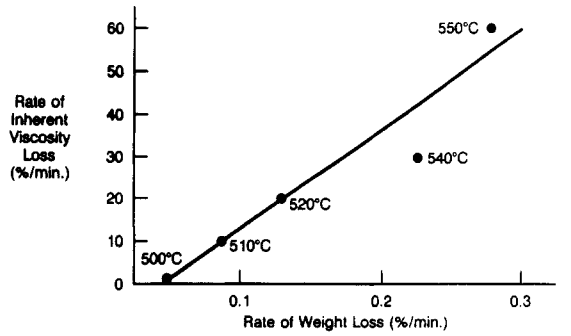


Figure 5. Correlation between rate of inherent viscosity drop for a PPTA polymerizate heated beyond the optimum and rate of pyrolytic weight loss (from isothermal TGA) in nitrogen for various temperatures in the 500–550 °C range.

Figure 4 is approximately constant throughout the polymerization. Isothermal TGA curves for PPTA polymer in the same temperature range show a constant rate of pyrolytic weight loss during an extended initial period; from these average rate values (Table I), applied to the time necessary to attain maximum inherent viscosity in prepolymer polymerizations, it may be calculated that pyrolytic weight loss during this time is slight. A typical value of 0.35% weight loss would amount to an average loss of only 65 MW units per macromolecule for $\bar{M}_n$ = 23 000 (η_{inh} = 6.0 dL/g). On the basis of experiment, this has little adverse effect on capability to form polymer of high inherent viscosity. Table I shows that the calculated weight loss in the time for polymerization to maximum inherent viscosity is more or less constant at 0.35%; thus rate of pyrolysis is proportional to rate of polymerization.

The inherent viscosity drop with excessive heating (Figure 4) is more or less constant in the range 510–550 °C. If, as discussed, this is a measure of insolubilization by cross-linking and cross-linking, in turn, is a measure of chain branching (at gross levels), it may be deduced that branching in PPTA at elevated temperature takes place at a constant rate, depending on temperature. Figure 5 shows that rate of branching, as measured by rate of inherent viscosity loss, is proportional to rate of pyrolytic weight loss.

There are thus three apparently independent processes—polymerization, pyrolysis, and chain branching—which proceed at significantly increased and constant rates above certain broadly similar threshold temperatures (500, 500, and 450 °C, respectively) in the solid-phase DPA–PPD polymerization. These must be accounted for in a consideration of the polymerization mechanism.

While temperature is the main experimental variable affecting polymerization rate, several other factors can have a significant influence (Figure 6). Catalysis by sodium methoxide (0.1% by weight), one of the most potent catalysts uncovered for the reaction of DPT with PPD, reduced the polymerization time for formation of maxi-

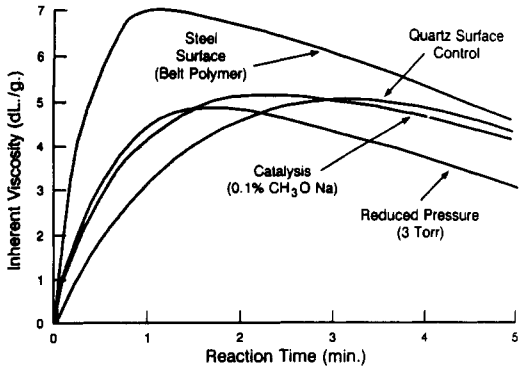


Figure 6. Effect of (a) a catalyst, (b) reduced pressure, and (c) rate of heat supply (steel versus quartz reaction surface) on polymerization of PPTA prepolymer at 500 °C by the tube furnace method as measured by inherent viscosity.

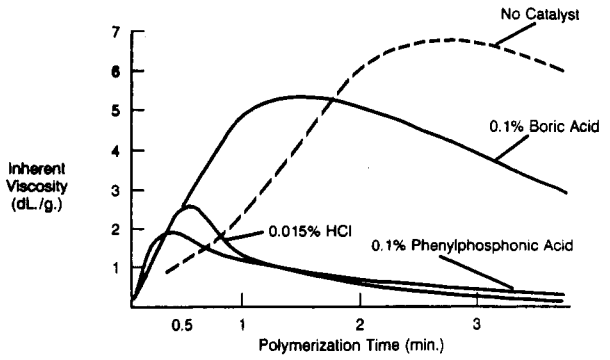


Figure 7. Effect of several acid catalysts on the polymerization of PPTA prepolymer at 520 °C by the tube furnace technique.

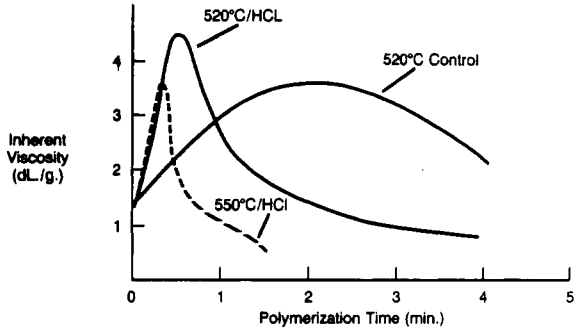


Figure 8. Effect of hydrogen chloride (25% by volume, in nitrogen) on inherent viscosity, on heating low-MW PPTA polymer (from PPD and terephthaloyl chloride) at 520–550 °C.

mum inherent viscosity at 500 °C by about 50% (Figures 4 and 6). Acids also catalyzed the rate of molecular weight growth of prepolymer. Figure 7 shows the effects of boric acid, hydrochloric acid, and phenylphosphonic acid. These also accelerate degradative processes, approximately in the order of acid strength, such that inherent viscosity maxima fall short of those for the uncatalyzed control. (The HCl-catalyzed reaction was conducted in an atmosphere of HCl/nitrogen.) At higher concentrations of HCl, inherent viscosity levels exceeding those of the control were attained but there was a dramatic increase in the rate of inherent viscosity drop-off (Figure 8), indicating, once again, acceleration of degradation processes; with HCl this may well signify previously unconsidered chain cleavage.

When prepolymer was heated via the tube furnace technique under reduced pressure of 3 Torr, the time to maximum inherent viscosity values was reduced by 50% (Figure 6), an effect comparable with sodium methoxide catalysis, without reduction of inherent viscosity level. The effect was proportionately as effective at 475 °C as

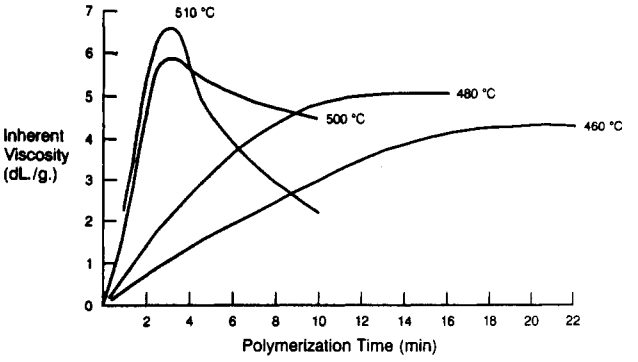


Figure 9. Polymerization of a monomer mixture of PPD (20 mol % excess) and DPT with a catalyst (0.0025% CH_3ONa) as followed by inherent viscosity changes.

it was at 500 °C. It is evidently the result of accelerated outward diffusion of byproduct phenol.

The rate at which heat can be supplied to the reactants is considerably greater in the belt apparatus than in the quartz tube procedure because of the comparatively greater thermal conductivity of steel. When the reactant contacts the quartz surface, the latter briefly drops in temperature as heat is supplied to the reactant before temperature is reestablished by heat from the furnace. This was reflected in a faster heat of polymerization in the belt apparatus (Figure 6) at 500 °C;[18] the inherent viscosity maximum was also higher by about 20%, which may reflect a relatively increased rate of polymerization relative to branching and cross-linking.

As an alternative to the prepolymer route, high-MW PPTA was also prepared in a single-stage polymerization, using either the tube furnace or steel belt method, from an intimate mixture of monomers and a suitable catalyst. Without catalyst, a monomer mixture contacted with a hot surface in the range of about 500 °C mostly evaporates before it can react; the result is about 20% yield of low-MW PPTA. With sodium methoxide catalysis, the monomers are converted to nonvolatile oligomer far faster than they can evaporate to give essentially quantitative conversion to high inherent viscosity polymer, which is quite comparable with that from prepolymer without catalyst. Inherent viscosity–time curves for sodium methoxide catalyst single-stage polymerizations are shown in Figure 9. In the terms of maximum inherent viscosity achieved it was advantageous to ensure intimate mixing of monomers and catalyst by premelting, resolidifying, and pulverizing. It was even more advantageous to use an excess of PPD over DPT up to about 20%. Volatile byproducts of the polymerization were phenol, unreacted PPD, a sublimable complex of PPD and DPT, and small amounts of DPT and 4′-amino-4-carbophenoxybenzanilide. Although it might be assumed that the PPD excess such would compensate for the faster rates of evaporation of PPD vs DPT, which would otherwise stoichiometrically unbalance the mixture severely, it certainly could not ensure stoichiometric equivalence of amine and phenyl ester groups in the polymerizate. Indeed it appears to ensure a predominance of amine ends. When 4′-amino-4-carbophenoxybenzanilide was polymerized in the presence of sodium methoxide, exact equivalence of end groups at all times was ensured but the inherent viscosity of the product was no higher than that with the unbalanced monomer mixture. Evidently stoichiometric equivalence of monomers is not essential.

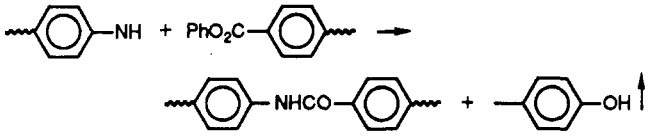
Alkoxides were the most potent catalysts tested for the single-stage DPT–PPD polymerization. Thus 0.001% sodium methoxide gave an inherent viscosity of 7.5 dL/g

in 1 min. Sodium methoxide and the other alkoxides were undoubtedly converted in situ under polymerization conditions by reaction with byproduct phenol into sodium phenoxide. Separate tests confirmed that the latter is a potent catalyst. Compared with other catalyst types, alkoxides gave the least amount of chain branching. Organic bases were ineffective.

As was observed in the two-stage prepolymer polymerization, acids also are strong catalysts but catalyze branching as well. An interesting case was amine hydrochlorides such as ammonium chloride or PPD·2HCl which effectively catalyze oligomerization of monomers to ensure minimum losses by volatilization and then volatilize out of the system (perhaps with dissociation) as the temperatures increase, so that they are not present to catalyze branching or other unwanted reactions at very high temperatures. Certain tin compounds such as stannous chloride and tin octanoate had considerable catalytic activity but they also facilitated cross-linking.

Discussion

Mechanism of Polymerization. In the polymerization to high MW of an aromatic diamine with an aromatic diester at temperatures of about 300 °C, as is possible with certain low-melting copolymers,[13] the critical requirements are (a) selection of phenyl esters as optimal leaving groups (as phenol) for interchange with arylamine groups



(b) catalysis to accelerate the otherwise sluggish phenolysis condensation, (c) efficient removal of byproduct phenol, (d) stoichiometric balance of NH_2 and CO_2PH end groups throughout the polymerization, and (e) facile translational movement within the matrix to facilitate encounters between reactive end groups. In the application of this reaction to PPD and DPT in the 350–400 °C temperature range, failure to attain high MW (η_{inh} > 3.5 dL/g) is attributable to immobilization of growing polymer, as previously suggested, at a modest MW level so that reactive ends can no longer encounter each other for reaction. An intense evaluation[9] of many catalysts with the idea of outpacing the immobilization processes has failed to break this barrier of limited MW. (The enormous potency of alkoxides in the single-stage DPT–PPD polymerization has already been discussed.) The untenability of this hypothetical rationale to explain the formation of high inherent viscosity PPTA formed in the ca. 500–550 °C region was demonstrated by conducting a polymerization in two stages (Figure 10). Low-MW prepolymer at 490 °C in 1–3 min gave inherent viscosity values of about 1.0–1.5 dL/g (data at long reaction times are discounted for present purposes because they reflect a large cross-linking contribution). When this material is cooled, the macromolecules are assuredly immobilized, and yet when the material is subjected to reaction conditions at a higher temperature of 550 °C, in 1 min the inherent viscosity jumped to nearly 6 dL/g.

The high-temperature phenolysis polymerization of PPTA differs from the lower temperature process just described in several important respects: (a) Very high inherent viscosities in the 500–550 °C region are attained without the use of a catalyst at all. (b) Whereas catalysts can accelerate the phenolysis reaction by a large factor at

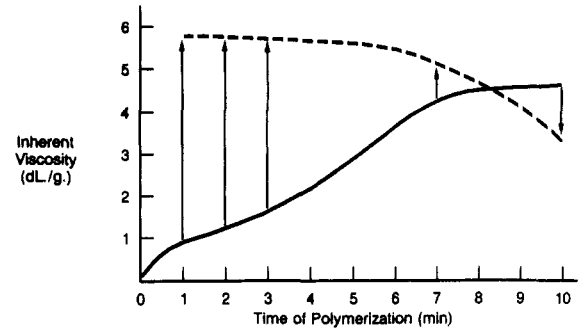
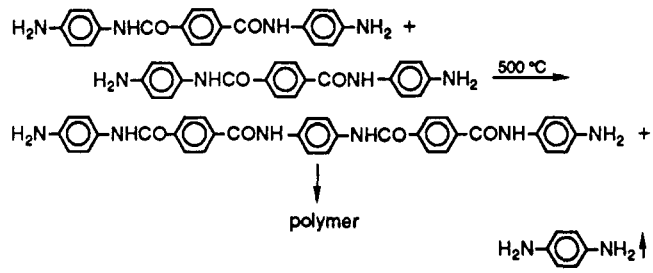


Figure 10. Two-cycle polymerization of PPTA prepolymer (a) at 490 °C (solid line), and (b) at 490 °C and then additionally at 550 °C/1 min.

low temperature, around 500 °C the rate of polymerization of the uncatalyzed process is little more than doubled. (c) There is no measured and progressive increase in polymerization rate as temperature is increased but rather there is an upsurge beyond a certain threshold in the region of 500 °C to high inherent viscosity levels. It is more than coincidence that the thresholds for the onset of pyrolytic degradation of PPTA and for accelerated chain branching are quite similar; all are at least 50 °C below the hypothetical melting point of PPTA. (d) The stoichiometric balance of NH_2 and CO_2Ph ends is not at all critical, and rather some excess of NH_2 is preferable for maximization of polymer MW.

Germane to the issue of polymerization mechanism were certain observations that PPTA polymer of significant MW is formed at ca. 500 °C (but not at ca. 400 °C) when NH_2 but not CO_2Ph ends are present (although the latter is necessary for highest MW). Thus, a completely amine-ended oligomeric species, diaminoterephthalanilide, forms PPTA for $\eta_{inh} \sim 1$ dL/g when heated at 500 °C.



This can only occur by interchange of NH_2 with an amide group to release PPD as a byproduct of condensation, and this ultimately volatilizes out of the system for a net gain of one amide group. PPD no doubt can undergo a sequence of other interchanges before it leaves the system, unlike phenol, and thus is not a very efficient leaving group; hence inherent viscosity of the formed polymer is low. Another example of PPTA MW growth, without the intermediacy of CO_2Ph groups, was heating of low-MW polymer (η_{inh} = 1.3 dL/g) containing NH_2 and COCl ends (from PPD and terephthaloyl chloride) for 1 min at 550 °C whereby η_{inh} rose to 3.3 dL/g. When this polymer was treated with sodium phenoxide in solution to convert COCL ends to CO_2Ph ends, the 550 °C/1 min treatment provided exactly the same inherent viscosity value, because PhOH is not superior to HCl in its ability to diffuse out of the system. Again, in combinations of NH_2 and CO_2H ends the latter groups are undoubtedly lost by decarboxylation to form an inert benzoyl end, so that the byproduct of polymerization is again the rather inefficient leaving byproduct, PPD.

The threshold temperature range beyond which PPTA polymer chain growth, pyrolytic decomposition, and chain

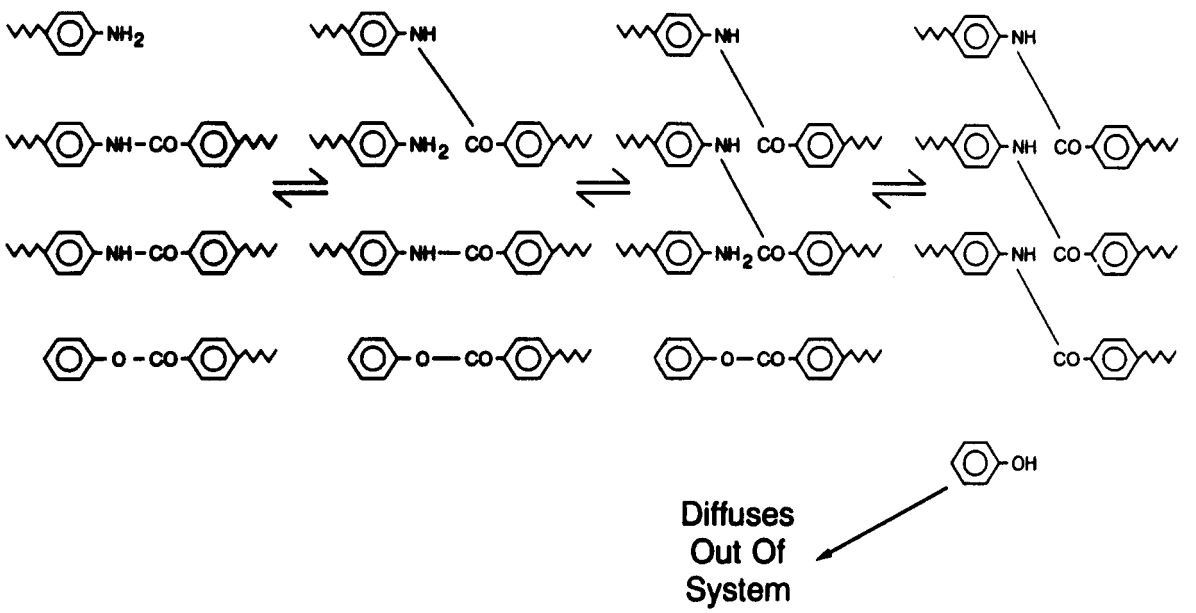


Figure 11. Interchange reactions leading to net gain of one amide linkage and elimination of one phenol molecule.

branching all accelerated is best interpreted as the point at which the macromolecules start to acquire enough segmental mobility so that amide interchange with NH_2 ends and the other undefined processes are no longer inhibited. It has been observed with several polymers that macromolecular chain stiffness makes a definite contribution to thermal stability, e.g., as in the comparison of PPTA and MPIA, undoubtedly by delaying the onset of segmental encounters that result in pyrolytic cleavage.

In the high-temperature solid-phase polymerization of PPTA in the region of 500 °C, where there is sufficient energy and segmental mobility for free interchange between amine ends and adjacent amide groups, the amine ends effectively "move" through the matrix by this process. Ultimately a small molecule is released and diffuses out of the system with the net gain of one additional amide linkage. This can occur most easily if the amine end encounters a phenyl ester group to release a readily diffusible phenol molecule as shown in Figure 11. In the case where there is an excess of amine ends, as is probably the situation in the single-stage PPTA polymerization from monomer, after the bulk of the phenyl ester groups has been eliminated by interchange, there can be continued MW increase by elimination of PPD. There is thus no necessity for amine and CO_2Ph end groups to be stoichiometrically balanced, but it is advantageous if the imbalance is toward excess amine rather than vice versa. The function of catalysts in the high-temperature phenolysis polymerization is simply a facilitation of the amide interchanges. The rate-limiting process appears to be diffusion of phenol or other byproducts out of the system. The accelerative effect of reduced pressure has been mentioned. With diffusion as the basic controller of polymerization rate the spectacular effectiveness of alkoxides at lower temperatures (manifested in phenolysis interchanges) cannot greatly influence the overall polymerization rate at high temperatures where amide interchange is already very fast.

Mechanism of Chain Branching. Compared with linear PPTA prepared by low-temperature solution polymerization, high-temperature PPTA in dilute sulfuric acid shows abnormally high viscosity at low shear and high sensitivity of viscosity to increasing shear. Such behavior is characteristic of branched polymers. An empirical but nevertheless useful method of summarizing

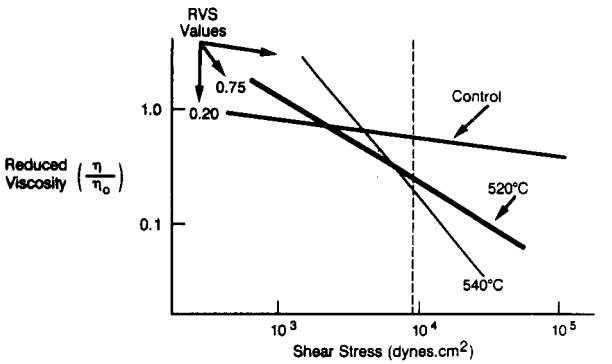


Figure 12. Anomalous slopes of reduced viscosity versus shear stress for high-temperature PPTA as a 3.5% solution in sulfuric acid compared with a linear PPTA control made by solution polymerization. η is the bulk viscosity at any given shear rate; η_0 is the bulk viscosity as a fixed value of very low shear rate.

and comparing the rheological behavior, and hence assessing degree of branching, is in terms of reduced viscosity slope (RVS). Where η is bulk viscosity of a 3.5% solution of polymer in sulfuric acid at a given shear rate and η_0 is bulk viscosity measured at the lowest shear setting of a Brookfield viscometer, η/η_0 is the reduced viscosity. RVS is the slope of reduced viscosity–shear rate curves at an arbitrarily chosen shear rate of 10^4 dyn/cm^2. Examples of such curves for linear PPTA and high-temperature polymers made at 520 and 540 °C are shown in Figure 12; respective RVS values are 0.20, 0.75, and 1.6. Anomalous solution behavior of 3.5% concentration is magnified at the 20% concentration preferred for solution spinning of PPTA. Experience has shown that acceptable commercial spinnability requires RVS values of less than 0.6. In the high-temperature, solid-phase synthesis RVS increases with reaction temperature, heating time, and presence of catalysts. It has become clear from a thorough examination of polymerization conditions that the high-temperature polymerization of PPTA is inevitably accompanied by an unacceptable level of chain branching. Even though the actual frequency of branching is low, its adverse effect on solution rheology is profound. Indeed the frequency of branching that produces cross-linking and insolubilization is also surprisingly low. A low level of branching also exerted a surprisingly large effect on the melting point of 19% solutions of PPTA in sulfuric acid in depressinng it

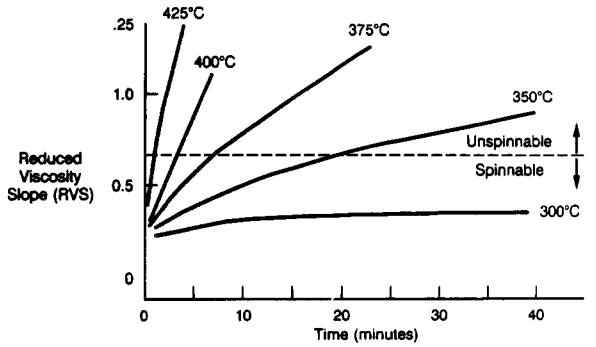


Figure 13. Development of branching in linear PPTA (inherent viscosity = 9 dL/g, by solution polymerization) on heating at various temperatures under nitrogen; branching is measured in terms of reduced viscosity slope.

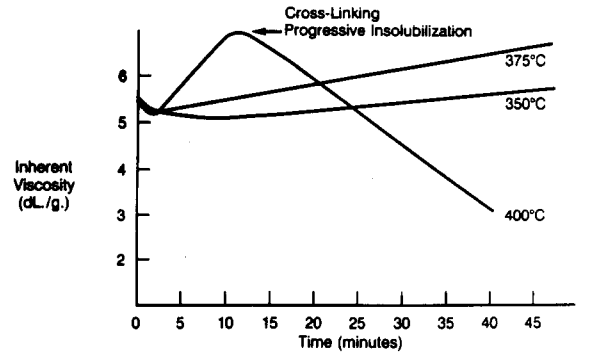


Figure 14. Effect of heating linear PPTA polymer in nitrogen on inherent viscosity.

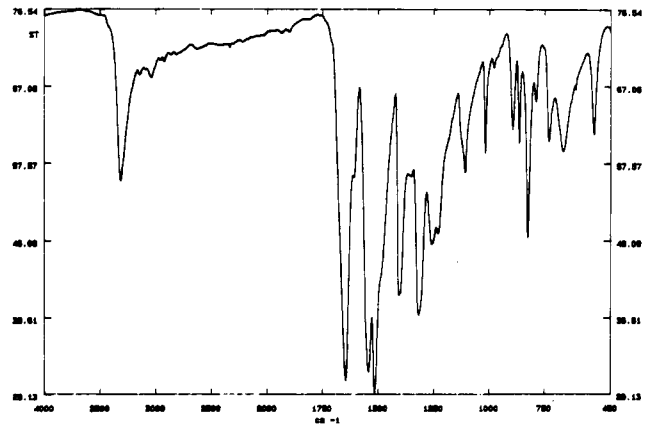


Figure 15. FTIR spectrum of PPTA prepared by phenolysis at 720 °C.

from 77 °C (for unbranched polymer) to 55–62 °C.

Although chain branching seems to accelerate above a threshold temperature of about 450 °C (Figure 3), it does proceed at a significant rate at lower temperatures. To separate branching processes from ongoing polymer chain extension, the development of branching in linear PPTA on heating was examined. A very high MW linear polymer of inherent viscosity of 9 dL/g was chosen to minimize the possibility of end-group effects in branching. The development of branching when this polymer was heated at various temperatures is illustrated in a plot of RVS against heating time (Figure 13). It is clear that excessive heating at temperatures above about 325 °C could produce sufficient branching as to render the polymer unspinnable. The rate of branching increased enormously as temperature was increased. At 400 °C, given sufficiently long exposure time, cross-linking occurred (Figure 14), indicated by an apparent reversal from inherent viscosity increases to decreases.

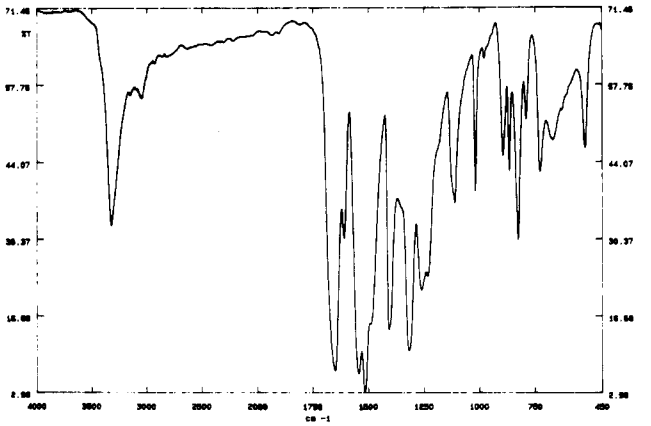
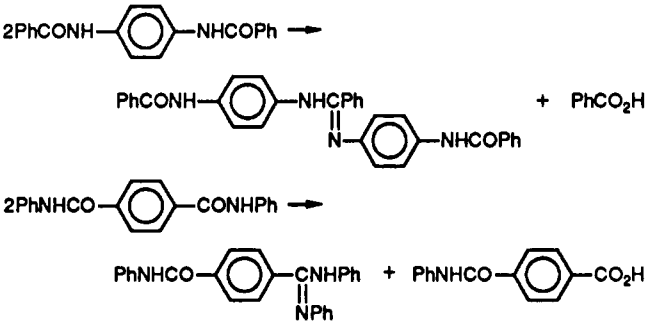


Figure 16. FTIR spectrum of PPTA prepared by solution condensation for manufacture of Kevlar aramid fiber.

Table II
Formation of Methyl Benzoate in the Methanolysate of PPTA

polymn conditions	methyl benzoate, ppm
425 °C/50 s/steel surface	0
450 °C/50 s/steel surface	0
475 °C/50 s/polymer tube	208
535 °C/5 min/polymer tube	358
550 °C/40 s/tube furnace	473
550 °C/60 s/tube furnace	873
soln polymn in amide solvent	0

High-temperature PPTA was indistinguishable from the low-temperature, linear PPTA used in the manufacture of Kevlar aramid fiber by ordinary analytical tools such as IR, DSC, DTA, TGA, or WAX. Figures 15 and 16 show the FTIR spectra of each type of PPTA, respectively, even for overheated polymer showing diminished solubility characteristic of branching. Since branch points are thus undetectable by FTIR spectra, they must be present in very low quantities indeed relative to the amide groups. When branched polymer was broken back to its monomeric units by methanolysis in HF and the methanolysate was analyzed by chromatography, no units identifiable directly as branch points were found. There was, however, an appreciable content of benzoic acid units, identified as methyl benzoate, which seemed to parallel the degree of branching indicated by RVS (Figure 12). The methyl benzoate content increased with polymerization temperature (Table II). The benzoic acid presumably originated in the disproportionation reaction of two amide groups in adjacent macromolecules. The occurrence of this reaction was demonstrated by analysis of the reaction products formed by extended heating of model compounds, *p*-phenylenedibenzamide or, alternatively, terephthalanilide, at 350 °C. It may be concluded that branch points are trifunctional amidines.



The absence of branching residues in the methanolysate

of branched PPTA is obviously due to the fact that amidine groups themselves are destroyed under methanolysis conditions. The presence of benzoic acid residues mentioned above is explainable in terms of the free CO_2H ends produced in the disproportionation associated with amidine formation are decarboxylated at high temperatures so that methanolysis produces a benzoic acid rather than a terephthalic acid residue. This rationale would indicate that even under the most severe branching conditions shown in Table II, the methyl benzoate level is indicative of a very low amidine content in the polymer of less than 1% of all groups joining phenylene rings. This is consistent with FTIR information. With this understanding of the nature of branching in PPTA, attempts were made to diminish branching by preferential hydrolysis of amidine branches. Some reduction in branching could be effected but not without significant hydrolysis of amide linkages as well. It has been remarked earlier that branched PPTA is a darker color than the linear polymer; this may be associated with the production of conjugatable C=N-amidine links.

Summary and Conclusions

PPTA has been prepared in high MW, as judged by inherent viscosity, by raising either a PPD–DPT–catalyst mixture or a low-MW PPD–DPT prepolymer to about 500–550 °C for a short time by novel techniques. The polymerization mechanism involves the acquisition of sufficient macromolecular segmental mobility above a certain threshold temperature range of about 475 °C to permit the facile interchange of amino ends with adjacent amide groups. In this way amine groups "move" through the matrix until interchange ultimately releases a moiety that diffuses out of the system with the net creation of an additional amide link. The most readily diffusible such moiety is phenol but other species, notably PPD, may likewise be eliminated. This high-temperature PPTA is inevitably associated with a degree of chain branching that, though not detectable by usual methods, has a profound adverse effect on the rheology of polymer solutions in PPTA from the point of view of practical fiber spinning. Model compound studies indicated that branching was the result of disproportionation between two amide groups to create a trifunctional amidine unit.

Acknowledgment. K. K. Likhyani reduced to practice and demonstrated the operation of the steel belt polymerizer. The contributions of A. H. Frazer and L. E. Seufert in the field of solid-phase PPTA polymerization are acknowledged.

References and Notes

(1) Arkin, M.; Strazielle, C. *Makromol. Chem.* **1976**, *177*, 581.
(2) Schaefgen, J. R. (Du Pont), unpublished work.
(3) Gardner, K. H. (Du Pont), unpublished work.
(4) Jaffe, M.; Jones, R. S. High-Performance Aramid Fibers. In *Handbook of Fiber Science and Technology: High Technology Fibers—III. Part A*; Lewin, M., Preston, J., Eds.; Marcel Dekker, Inc.: New York, 1985.
(5) Morgan, P. W. *Condensation Polymers: By Interfacial and Solution Method*; Interscience: New York, 1965.
(6) Bair, T. I.; Morgan, P. W. U.S. Patent 3,673,143, 1973.
(7) (a) Fitzgerald, J. A.; Likhyani, K. K. U.S. Patent 3,850,888, 1974. (b) Memeger, W. (Du Pont), unpublished work.
(8) Vollbracht, L.; Veerman, T. J. Ger. Patent 2,605,531, 1976.
(9) Frazer, A. H. (Du Pont), unpublished work.
(10) Silver, F. M. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3519.
(11) Shin, H. U.S. Patent 4,009,153, 1977.
(12) Sikkima, D. J. U.S. Patent 4,758,651, 1988.
(13) Sweeny, W. Eur. Patent 388,203, 1990.
(14) Calundann, G. W.; Charbonneau, L. F.; East, A. J. U.S. Patent 4,351,917, 1984.
(15) Jones, R. S. U.S. Patent 3,753,957, 1973.
(16) Blume, R. C. U.S. Patent 3,558,571, 1971.
(17) Memeger, W. *Macromolecules* **1976**, *9*, 198.
(18) Likhyani, K. K., unpublished work.