

A Processable Prepolymer for the Preparation of a Stable Conductive Polymer

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Synopsis

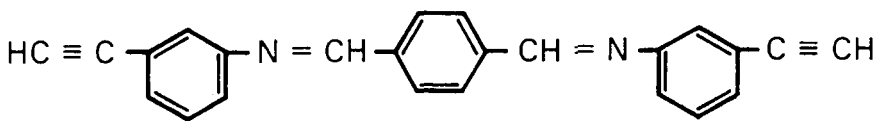
We recently reported¹ the synthesis and polymerization of a completely conjugated acetylene terminated prepolymer into an intrinsically conducting organic polymer. Although this polymer exhibited high thermal and environmental stability, its processing window, i.e., the temperature at which it melted vs. the temperature of the highly exothermic cure, was narrow. We now report the synthesis and polymerization of an isomer of this acetylene terminated material. This change in structure resulted in a 63°C decrease in the melting point (87 vs. 150°C) that provides a more than adequate liquid range between melting and the on-set of curing. Along with the greatly improved processing, this isomer results in an intrinsically conducting, thermally and oxidatively stable polymer equivalent to the original material.

INTRODUCTION

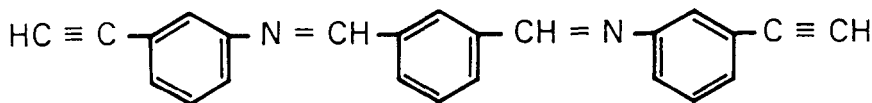
We recently described¹ a meta-para-meta (mpm) isomer of an acetylene terminated prepolymer (Scheme I, structure 1) used for the preparation of an intrinsically conducting polymer with high stability to very aggressive environments (boiling water for 1000 h or temperatures up to 400–500°C for several hundred hours in an oxygen free atmosphere). The synthesis of this isomer was partly based on the fact that the two materials (3-aminophenyl-acetylene and terephthalaldehyde) used in the synthesis were commercially available. It was anticipated that this availability and the potentially superior performance of the material would lend to its commercialization; and indeed, some industrial interest has been shown in developing and producing this material.^{*,2}

The prepolymer melts at 139 or 150°C depending on the polymorphic structure obtained in its synthesis or recrystallization. Since the cure of the polymer begins immediately after melting (see Fig. 1) and produces a very energetic exotherm (783 J/g, 62.2 kcal/m) that peaks at approximately 210°C, care must be taken to ensure that the temperature does not increase above 160–165°C during the first hour of the cure. The larger the sample, the more care is needed since heat buildup in the center of the liquid melt may not be dissipated sufficiently to prevent localized temperature increases past the critical value. In particular, care must be taken on transferring the sample into a preheated oven where the draft from opening the oven door may cause the control thermocouple to apply heat and overheat the sample after the door is closed. Superimposed upon this is the need to not let the sample partially recrystallize by keeping the temperature too close to its melting point. The unmelted sample will not cure with the melted portion, thereby

*Under development by National Starch and Chemical Corp., Bridgewater, NJ 08807, as Thermcon 1000.



STRUCTURE 1 - Meta-para-meta (mpm) Isomer



STRUCTURE 2 - Meta-meta-meta (mmm) Isomer

Scheme I.

introducing flaws in the final material. Nevertheless, one can prepare good samples with the proper technique as described in the earlier paper.¹

An additional approach not emphasized in that paper is to partially b-stage the resin. The degree of b-staging that can be imparted to the prepolymer before its viscosity becomes too high for handling does not sufficiently reduce the energy of the cure exotherm to prevent the highly exothermic reaction and decomposition that occurs if the temperature is still allowed to increase too rapidly. b-Staging helps by lowering the resolidification (recrystallization) temperature, e.g., as low as 100°C. Thus, after proper b-staging (e.g., 30 min at 155°C), the cure temperature can be lowered to 140–145°C for a slower, safer initial processing without concern for partial or localized crystallization of portion of the sample. After 2–3 h at this lower temperature, the cure may be safely taken to the higher temperatures as described in Ref. 1.

The subject of this paper is to describe another approach for increasing the processing window between the temperatures of melting and exothermic cure.

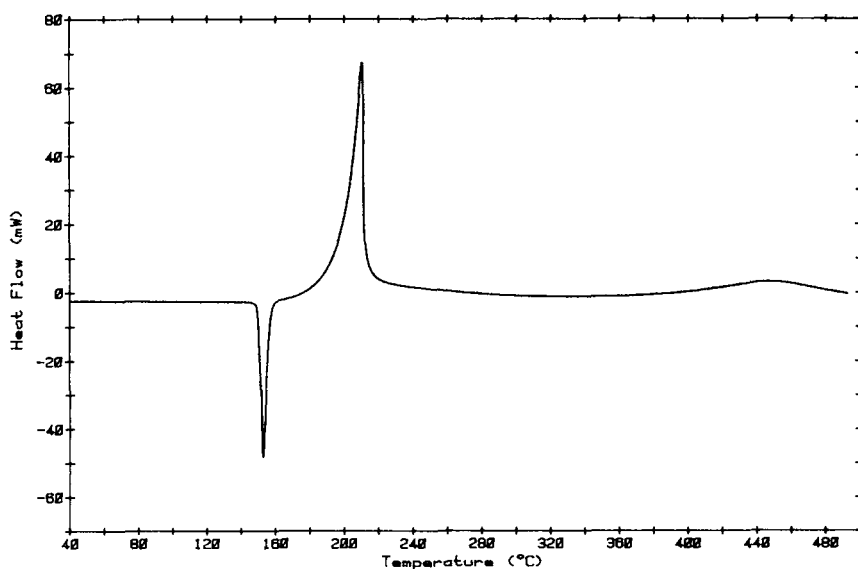
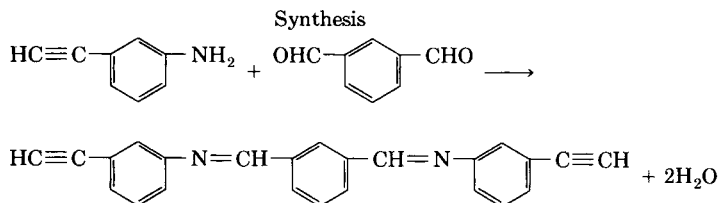


Fig. 1. DSC scan of structure 1 (mpm) illustrating the narrow processing window between sample melting and the highly exothermic cure. Heating rate 10°C/min; nitrogen atmosphere at 80 mL/min.

An initial approach was to control the exothermic cure reaction by use of inhibitors, either to move the reaction to higher temperature or to moderate the energetics of the reaction(s). This approach was unsuccessful; therefore, we turned our attention to modifying the melting point of the system by the synthesis of an isomeric structure of 1, *N,N'*-(1,3-phenylenedimethylidyne)bis(3-ethynylaniline), structure 2 (mmm), as described below.



The 3-aminophenylacetylene is obtained from National Starch and Chemical Corp. and was used as received. The isophthalaldehyde was obtained from Fluka, dissolved in toluene and separated from a toluene insoluble contaminant by filtration. A solution of isophthalaldehyde (9.98 g, 74.4 mmol) in 150 mL toluene was added dropwise over 1 h to a stirred, refluxing solution of 3-aminophenylacetylene (18.28 g, 156.0 mmol—4.84% excess) in 100 mL toluene containing 0.02 g of *p*-toluenesulfonic acid as a catalyst. The reaction was continued for 24 h during which 2.00 mL (theory 2.68 mL) of water was collected in the Dean-Stark trap. The reaction mixture was cooled to room temperature and filtered to remove a few milligrams of insoluble residue. The solvent was evaporated to yield 27.4 g of crude product contaminated with excess 3-aminophenylacetylene and possible unreacted starting materials and byproducts. The product at this stage is a very viscous, dark brown liquid which over a period of several days hardens into a glassy material.

The product is purified by column chromatography. A solution of 27.04 g crude product in 50 mL toluene is added to a 2 1/4 in. i.d. column filled to a height of 4 in. with acidic Al_2O_3 and eluted with toluene. After removing the solvent, a viscous liquid is obtained which solidifies after 1 h into a bright yellow solid. Further drying in a vacuum oven at 60°C for 3 h under 1 mm Hg gave 16.72 g (68% yield) of purified material, mp = 86–87°C. The elemental analysis results were:

ANAL. Calcd C = 86.71%, H = 4.68%, N = 8.43%. Found: C = 86.19%, H = 4.96%, N = 8.04%.

Table I summarizes the important proton NMR and IR spectra absorptions for the isomers, structures 1 and 2. As discussed in the earlier paper,¹ structure 1 appears to exist in two polymorphic forms and the data in Table I are for the lower melting (139°C) form. We do not have evidence that structure 2 (all meta isomer) exists in more than one crystalline form. Indeed, this isomer is very difficult to crystallize. For example, attempts to recrystallize from isopropyl alcohol usually leads to a separation of an oily liquid on cooling the hot solution. Generally, a seed crystal must be added to initiate crystallization. The solubility of the all meta isomer is very high in toluene and ethyl alcohol compared to the mpm isomer which could efficiently be recrystallized from these solvents.

TABLE I
Comparison of Spectral Properties of Structures 1 and 2

	mmm Isomer	mpm Isomer
	Proton NMR absorption ^a	
—C≡C—H	3.10 (s) ppm	3.08 (s) ppm
—N=C—H	8.54 (s) ppm	8.51 (s) ppm
1,3-Ar-H	7.06–8.50 (m) ppm	7.14–7.60 (m) ppm
1,4-Ar-H	—	8.02 (s) ppm
	Infrared Absorption ^b	
—C≡C—H	3290, 3276 cm ⁻¹ (s)	3275, 3265 cm ⁻¹ (s)
—C≡C—	2108 cm ⁻¹ (w)	2110 cm ⁻¹ (vw)
—N=C—	1626 cm ⁻¹ (s)	1622 cm ⁻¹ (s)
—N=C—H	2891, 2870 cm ⁻¹ (m)	2875, 2860 (w)

^aH-NMR absorption in CDCl₃, TMS reference; s = singlet, m = multiplet.

^bFT-IR absorption, KBr pressed pellet; s = strong, m = medium, w = weak.

DISCUSSION

Figures 1 and 2 show the DSC (differential scanning calorimetry) curves for mpm isomer (structure 1) and the meta–meta–meta (mmm) isomer (structure 2), respectively. The DSC for the mpm is for the high melting form (150°C), which is currently available.* (See footnote, p. 1921.) It is apparent that, immediately on melting, this isomer begins to cure and thus provides a very limited processing window. The material remains liquid for approximately 1 h at this melt temperature (150°C). In many process applications, having the prepolymer in the liquid phase for a longer period of time would be desirable.

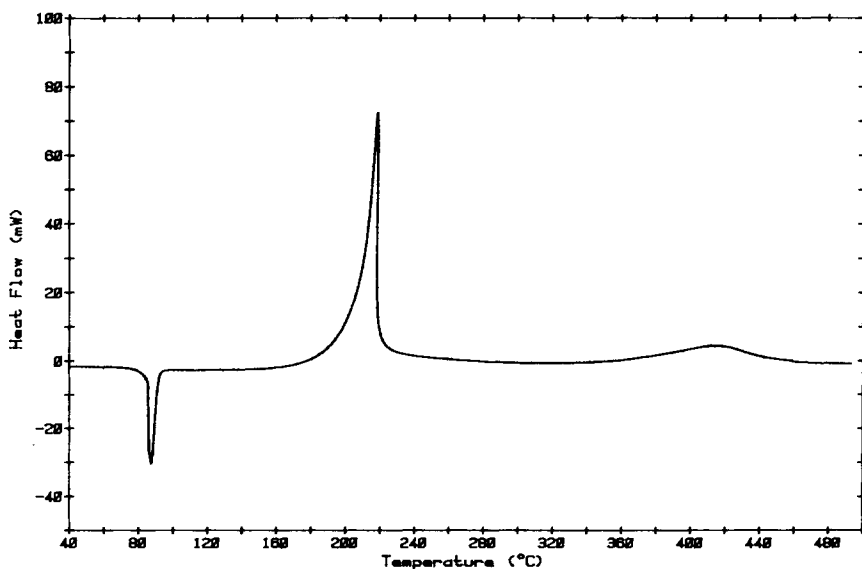


Fig. 2. DSC scan of structure 2 (mmm) illustrating the broad processing window between sample melting and the highly exothermic cure. Heating rate 10°C/min; nitrogen atmosphere at 80 mL/min.

Superimposed on the short liquid phase time is the highly energetic cure that peaks at approximately 210°C with a heat of reaction of 783 J/g (62.2 kcal/mol). If the temperature drifts much above 150°C due to insufficient temperature control, or self-heating of large samples resulting from the energetics of the reaction and poor heat dissipation in the bulk sample, the polymerization reaction will lead to charring, foaming, and decomposition.

Figure 2 shows the substantial decrease in the prepolymer melting point (the endothermic peak on DSC curve) of the all meta structure. The melting point, 87°C, is well below the initiation temperature for polymerization. Thus, the material can be kept in the liquid state at 120°C for prolonged periods without concern for solidification by polymerization or recrystallization. Based on the DSC curves, the polymerization is initiated at approximately 139°C for the mmm and mpm isomers. However, the heat of polymerization of the all meta isomer, 673 J/g (53.5 kcal/mol), appears to be approximately 110 J/g less than the para-containing isomer, and the exotherm maximum occurs approximately 9°C higher at 219°C. These modified properties associated with the all meta isomer greatly improve the processing of the acetylene-terminated prepolymer.

POLYMERIZATION AND POST PROCESSING

The polymerization was carried out as described previously for the mpm isomer¹ except for the initial processing. During the initial stages of processing, the new isomer is melted at approximately 125°C and the temperature slowly brought to 145°C for 1 h, then to 150°C for 2 h. The remaining processing is as per the other isomer: The temperature increased and held at 200°C for 1 h, then at 250°C for 1 h, and finally at 300°C for 50 h. The cure is performed in an oven that is not protected from an air environment, and the sample shows little or no weight loss during the cure. It is believed that these prepolymers initially cure by a series of complex addition reactions which should be quite similar to those reported for other acetylene-terminated prepolymers.³ As would be expected for such a polymerization mechanism, the carbon, hydrogen, and nitrogen content of the initially cured polymer (150–300°C) did not change from the original values for the prepolymer. As emphasized,^{1,4} these are not necessarily optimum cure conditions, but a standard procedure used for comparative purposes for a number of materials under development in our laboratory.

After this initial cure, the material is removed from the aluminum planchet or mold in which it was prepared. At this stage, the polymer is nonconductive; but, by further processing at higher temperatures, conductivity can be introduced. Typically, the cured material is further heated under an inert atmosphere in a furnace. A stream of oxygen-free nitrogen or argon is passed through the furnace at a flow rate of 50 mL/min. The outlet of the furnace is restricted with a capillary tube to reduce back diffusion of air. The heating and cooling rates for the furnaces were approximately 0.5°C/min.

For comparative purposes, a standardized heating procedure was used in further processing the samples into conductive polymers. After the 300°C cure in air for 50 h, each sample was heated to 400°C for 100 h, 500°C for 100 h, 600°C for 100 h, etc. At the end of each 100 h treatment, the samples were

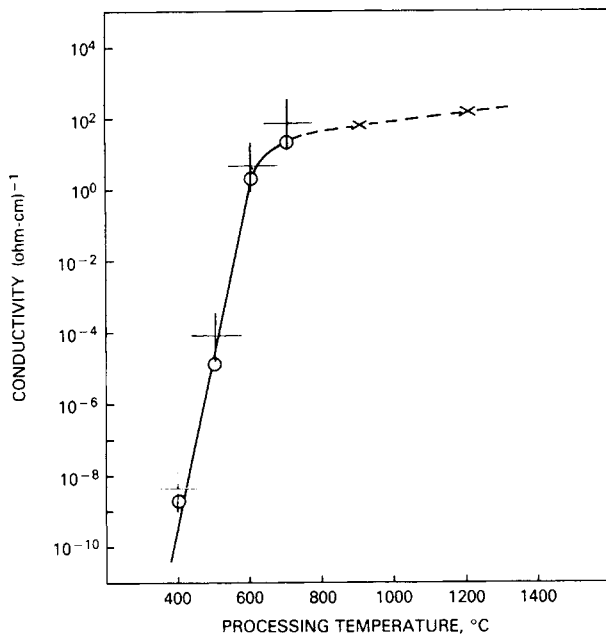


Fig. 3. Comparison of the post-processing temperature on the room temperature conductivity of structure 1 (mmp) (○, ×) and structure 2 (mmm) (+). The values represented by an × were for the sample processed for 5 h at that temperature rather than 100 h.

removed, and the conductivity and weight loss measured. Again these conditions are chosen for comparative purposes and are not necessarily optimum; and indeed faster processing conditions can be used.^{1,4}

Figure 3 shows the conductivity (measured by four-point probe technique described in Ref. 1, p. 975) of the mmm isomer superimposed on the original conductivity curve obtained for the mmp isomer.¹ Although the all meta system appears to have a slightly higher conductivity, from a practical point of view, the conductivity of the two isomers are the same for equivalent processing.

Similarly, Figure 4 shows a comparison of the weight loss observed for the two isomers during the high temperature processing. It can be observed that the all meta isomer possesses the same high thermal stability exhibited by the mmp isomer. As pointed out in Ref. 1, some shrinkage occurs during the high temperature processing. The shrinkage appears to be uniform in all directions, and the sample is a slightly smaller replicate of the original. To a first approximation, the linear shrinkage is slightly less than the corresponding percent weight loss; for example, after 100 h at 600°C the linear shrinkage was 11.7%.

As a further demonstration of the similarity between the two isomers, the thermogravimetric analysis (TGA) of the all meta isomer is compared to the mmp isomer in both nitrogen (Fig. 5) and air (Fig. 6) atmospheres. The samples had been previously cured at 300°C for 50 h and were analyzed as solid chips that were approximately of the same size and weight. The heating rate was 10°C/min and the gas (nitrogen or air) flow rate was 80 mL/min.

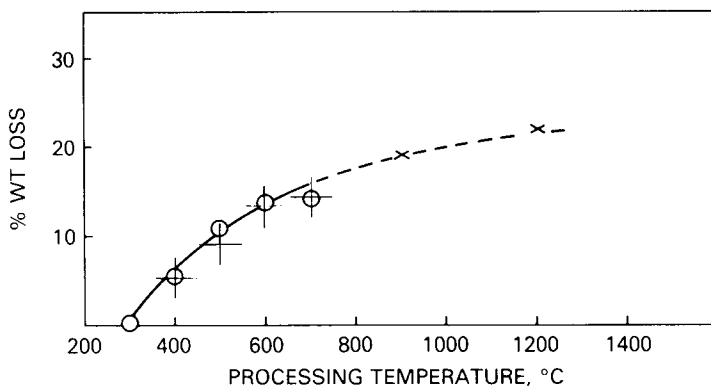


Fig. 4. Comparison of the post-processing temperature on the percent weight loss (nitrogen atmosphere) between structure 1 (mmp) (O, X) and structure 2 (mmm) (+). The values represented by an X were for the sample processed for 5 h at that temperature rather than 100 h.

Note that the weight loss scale is 84–112% for nitrogen and 0–150% for air measurements.

To approximately 450°C, the weight loss of 2–3% is mostly absorbed water.¹ Although the all meta isomer shows a smaller weight loss than the mmp isomer in both nitrogen and air, we don't believe that this represents a significant difference in their thermal and oxidative stabilities. The difference is, to a first approximation, fairly constant and is attributed to a slightly higher water absorption in the mmp isomer during exposure to the laboratory environment.

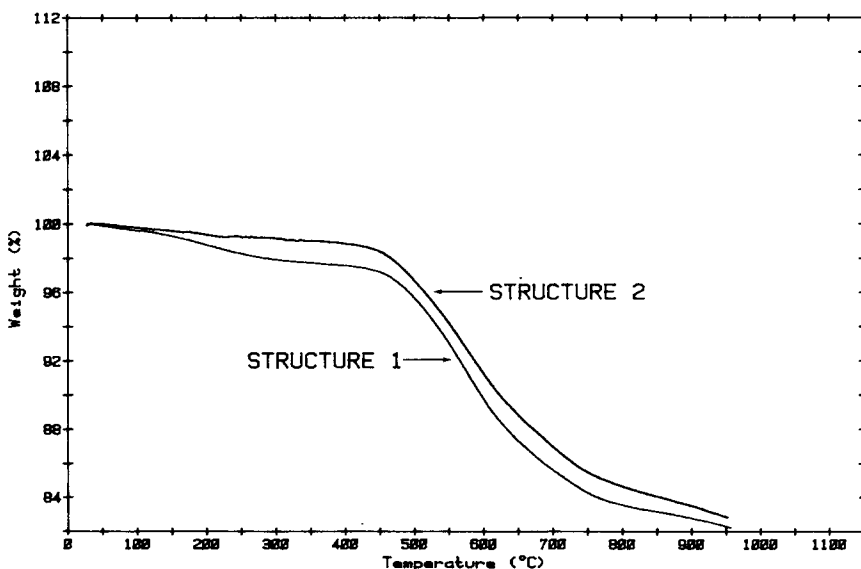


Fig. 5. Comparison of the TGA weight loss in nitrogen (after initial cure at 300°C for 50 h) between structure 1 (mmp) and structure 2 (mmm). Heating rate 10°C/min; nitrogen atmosphere at 80 mL/min; solid sample weight 11.63 mg for structure 1 and 10.16 mg for structure 2.

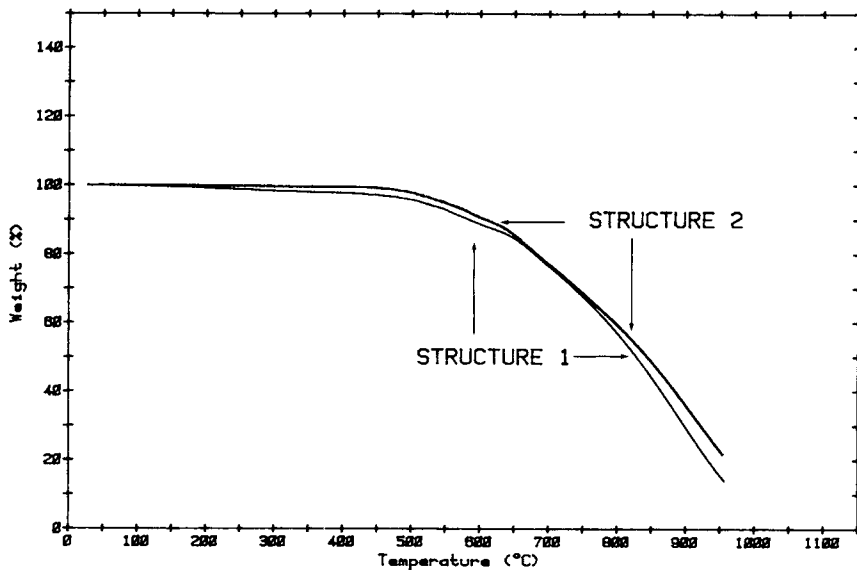


Fig. 6. Comparison of the TGA weight loss in air (after initial cure at 300°C for 50 h) between structure 1 (mpm) and structure 2 (mmm). Heating rate 10°C/min; air atmosphere at 80 mL/min; solid sample weight 51.89 mg for structure 1 and 50.98 mg for structure 2.

The volatiles given off during the high temperature processing (300–900°C) have been examined by FT-IR. Ammonia and methane are essentially the only products observed. Traces of carbon monoxide and carbon dioxide are also detected and attributed to a trace amount of oxygen in the carrier gas (nitrogen) used in the experiment. This oxygen results in a slight oxidation of the polymer at the higher temperature. Compounds such as toluene or benzene are not observed and examination of the reaction tube does not reveal the presence of higher molecular weight species or tars. Comments on changes in structure and C, H, and N content will have to await more detailed examination of these and other similar structures currently under study.

CONCLUSIONS

Studies have demonstrated that the acetylene-terminated prepolymer with an all meta structure (structure 2) has a conductivity and thermal stability equivalent to the mpm isomer (structure 1) described in an earlier paper. The all meta isomer, however, has a much lower melting point (87°C) and thus a broader processing window, i.e., melting point vs. temperature of exothermic cure. The much broader processing window is quite beneficial in certain applications. Although the two isomers can be interchanged from a performance consideration, the isophthalaldehyde used in the all meta synthesis is more expensive than the terephthalaldehyde used in the original synthesis. Thus, the cost of the all meta system may be more. Nevertheless, we have found that mixtures of the two isomers can be used to obtain a lower melting material with a broader processing window.

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References

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