Mass Spectrometric Analysis of Polymers Derived from *N*-Aryl-α-Amino Acid Initiators

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ABSTRACT: Previous studies have demonstrated that the interaction of carboxylic acids with aryl amines produces free radicals that can initiate the polymerization of acrylic monomers. *N*-Aryl-α-amino acids (NAAA) represent a special class of this type of initiator that combines in one molecule the carboxylic acid and aryl amine functionalities necessary for the generation of radical species. The mechanism(s) of radical formation in these molecules is thought to involve both electron transfer and hydrogen abstraction reactions that can occur by intra- and intermolecular pathways. Acrylic monomers, i.e., methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA), were activated with various amounts of several NAAAs. Specific NAAAs investigated include *N*-phenylglycine (NPG) and *N*-*p*-tolylglycine (NTG). Polymerization was conducted at ambient or near ambient temperatures, and the polymers then were analyzed by electron impact mass spectrometry. Results indicate that these polymers have end groups derived directly from the NAAA initiators. © 1997 John Wiley & Sons, Inc.* J Appl Polym Sci **65:** 561–565, 1997

INTRODUCTION

Adhesion between dental methacrylate polymers and hard tooth tissue has been achieved by the sequential application of acids as conditioners, *N*-aryl-α-amino acids as primers, and surface-active monomers as bonding resins.[1] Although some aspects of the mechanism of dental adhesion by this type of bonding system have been identified, a plausible explanation for the observed spontaneous interfacial polymerization of adhesive monomers has only recently been advanced.[2] It was shown that this spontaneous polymerization also occurred with a wide variety of dental acrylic monomers, such as methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA), that had been activated with both a variety of carboxylic acids (e.g., 2,4-dichlorobenzoic acid, trifluoroacetic acid) and aromatic amines (e.g., *N,N*-dimethyl-*p*-toluidine, *N*-phenylglycine). This polymerization mechanism may also explain the instability in solution of the addition reaction product of *N*-phenylglycine (NPG) and glycidyl methacrylate (GMA) and of the adduct of *N*-*p*-

Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the ADA Health Foundation or that the material or equipment identified is necessarily the best available for the purpose.

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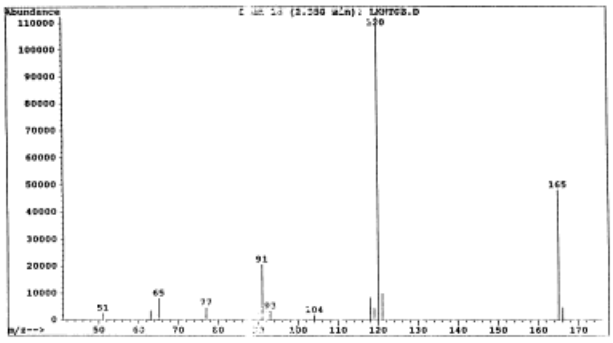


Figure 1 DIP-MS mass spectrum of NTG. The DIP was programmed for a temperature gradient from 50°C to 325°C at 20°/min. The ion source temperature was 300°C, electron energy 70 eV.

tolylglycine (NTG) and GMA. The mechanism(s) for these polymerizations appear to involve the formation of an unstable salt or complex between the carboxylic acid and amine groups, which then decompose to initiating radicals.[2] Also the addition of the *N*-aryl-α-amino acids, NPG and NTG, to acrylic monomers results in their gelation or polymerization.[3] It has been shown that NPG-GMA and NTG also can produce free radicals under oxidative conditions that are involved in initiating the polymerization of adhesive bonding resins.[4] Finally, it has been reported that free radical formation occurs by the sensitized decarboxylation of *N*-phenylglycine in the presence of (thio)-xanthene dye.[5]

The goal of this study was to enhance the understanding of the mechanisms behind the spontaneous free radical reactivity of these *N*-aryl-α-amino acids in order to maximize both their storage stability and to develop improved adhesives based on the observed polymerization-initiating

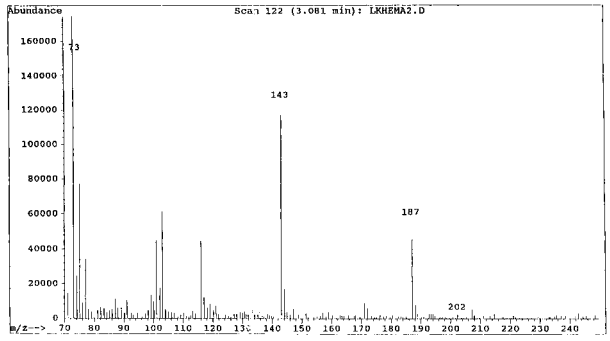
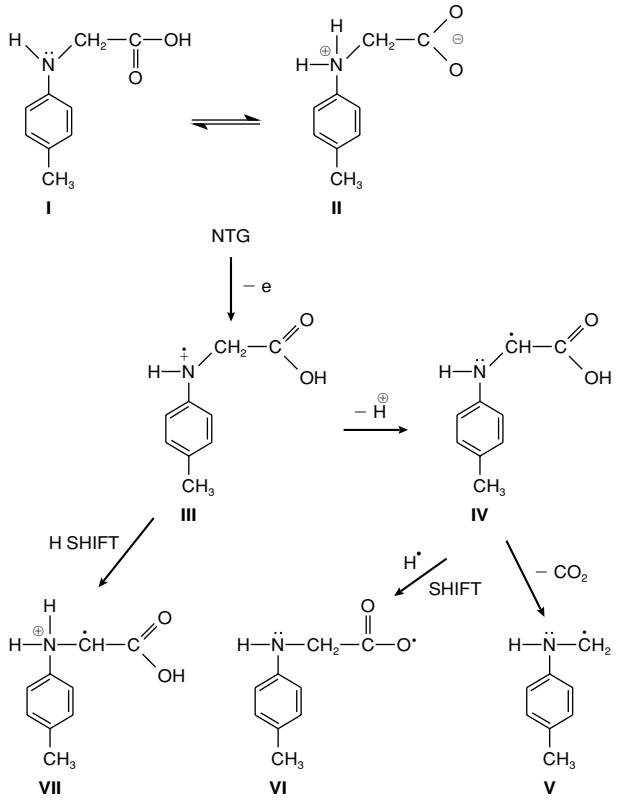


Figure 2 GC-MS mass spectrum of the TMS derivative of HEMA. GC Column: (Supelco fused silica SPB-5 capillary, 15 m, 0.25 mm i.d., 0.25 μm film thickness). The ion source temperature was 200°C, electron energy 70 eV.



Scheme 1 Radical-forming mechanisms for NTG initiated by a single electron transfer resulting from carboxylic acid-amine intramolecular interaction.

abilities. It was the specific purpose of the present study to investigate the characteristics of the initiating free radicals derived from NTG and NPG by mass spectrometric analysis of the electron impact fragmentation products of polymers formed with these initiators. This knowledge should aid in elucidating the mechanisms of polymerization of acrylic monomers by *N*-aryl-α-amino acids.

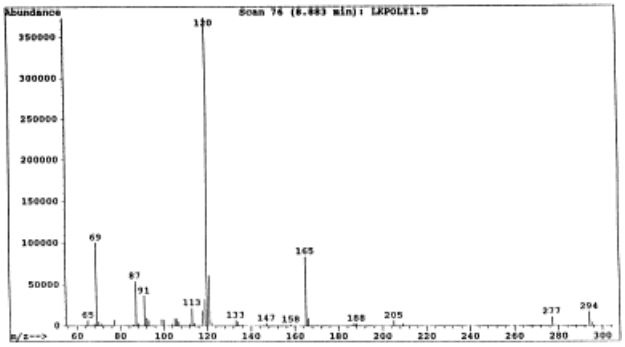
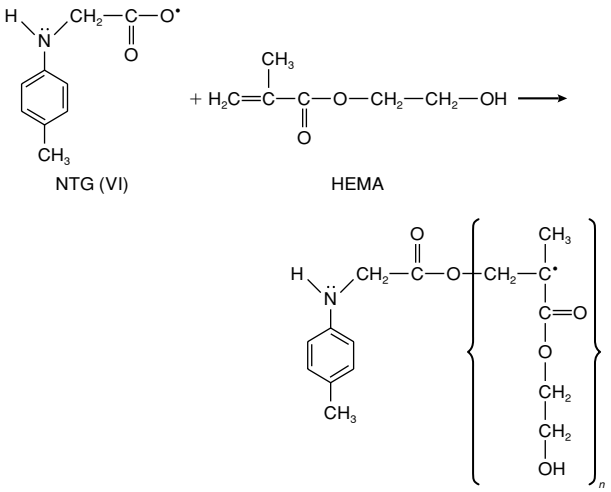


Figure 3 DIP-MS mass spectrum of NTG and HEMA reaction product. Same conditions as Figure 1.



Equation 1 The possible reaction of NTG radicals (VI) with the vinyl group of HEMA that would lead to the observed molecular ion.

EXPERIMENTAL

All the materials were from commercial sources and used as received except NTG. NTG was synthesized at NIST.[6] MMA and NPG were obtained from Aldrich and HEMA and BZMA from Esschem. Bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and acetonitrile were from Pierce. Typical experimental procedures used in this study are outlined below.

NTG (1×10^{-4} mol) was mixed with HEMA (5×10^{-3} mol) in a glass vial until the NTG was well suspended. Aliquots (ca. 4–6 μL) of the mixture were distributed into small glass capillary tubes and left at ambient temperature to allow polymerization to progress. In addition, MMA solutions of 2.6% NTG were prepared. Similarly, a solution of NTG (2%) in benzyl methacrylate (BZMA) was prepared and analyzed. (All percentages are on a mass basis).

Mass Spectrometry

The reagent materials were characterized first by mass spectrometry; then the polymerized samples were analyzed at several time intervals after mixing by direct insertion probe mass spectrometry. (DIP-MS) analyses were undertaken with a Hewlett-Packard Model 5988A mass spectrometer equipped with a Hewlett-Packard direct insertion probe (DIP). The DIP was programmed for a temperature gradient from 50°C to 325°C at 20°/min (held at 10 min at 325°C). The ion source temperature was 300–325°C, the electron multiplier was set at 2000 V, and the electron energy was set at 70 eV.

Gas Chromatography-Mass Spectrometry (GC-MS)

Samples of HEMA and polymer of (HEMA + NTG) were trimethylsilylated in Teflon-capped Hypovials with 0.1 mL each of BSTFA and acetonitrile 1 : 1 by heating for 15 min at 140°C. Approximately 1 μL of each derivatized sample was analyzed by capillary GC-MS. GC-MS separations were done on a Hewlett-Packard (HP) 5890 series gas chromatograph fitted with a Supelco fused silica SPB-5 phase capillary column (15 m, 0.25 mm i.d., 0.25 μm film thickness) with helium carrier gas (30 kPa head pressure, 30 s to 90 split). Detection was performed on an HP 5970 mass selective detector (50 amu/scan to 800 amu/scan, electron impact ionization at 70 eV) maintained at a source temperature of 250°C. The injection port and GC-MS interface were both maintained at 250°C.

RESULTS AND DISCUSSION

NTG, MMA, HEMA, and BZMA were analyzed by mass spectrometry separately under the same experimental conditions as their products.

NTG gives a stable molecular ion, $M^{+\bullet}$, at m/z 165, as shown by the intense peak in the mass spectrum (Fig. 1). In the displayed spectrum, loss of COOH leading to m/z 120 ion is a common major cleavage product. Also, the ion at m/z 91 was due to elimination of ($HN—CH_2—COOH$) from the $M^{+\bullet}$ ion.

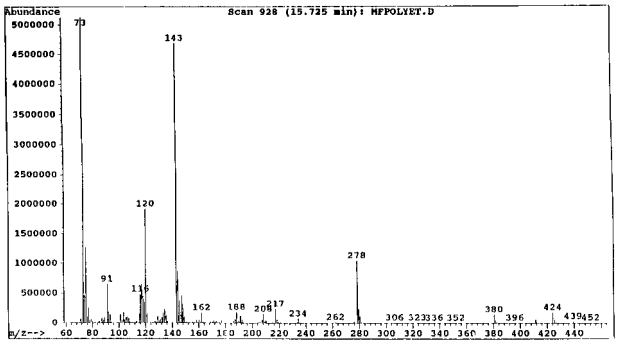
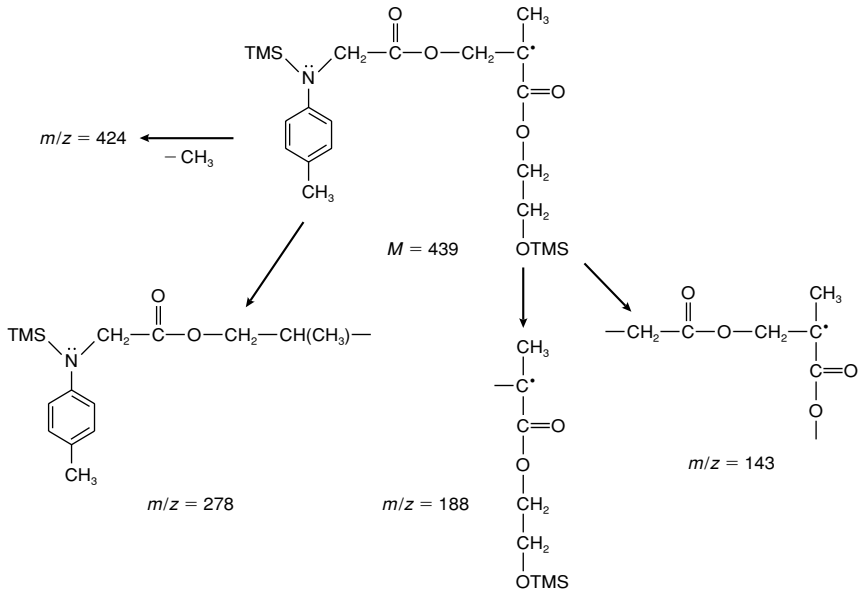


Figure 4 GC-MS mass spectrum of TMS derivative of HEMA and NTG. Same conditions as Figure 2.



Scheme 2 Mass spectrum fragmentation of derivatized (HEMA + NTG) for Figure 4.

The TMS derivative of HEMA was analyzed by GC-MS. The characteristic ion resulting from CH_3 loss, $(M\text{-}15)^+$, was observed at m/z 187 (Fig. 2).

The reaction of NTG with MMA, HEMA, and BZMA most likely is initiated by transfer of one of the electrons of the free electron pair from the nitrogen atom. This electron transfer can occur by intra- and intermolecular pathways (Scheme 1). A plausible pathway for the formation of the free radical (IV) involves removal of a hydrogen from the α-carbon in NTG (III). The free radical (V) can form by loss of CO_2 from (IV). The formation of the carboxyl radical (VI) is possible by a H shift from —COOH to the α-carbon in IV. Also, free radical VII could possibly form by a H shift from α-carbon to the amino group in III.

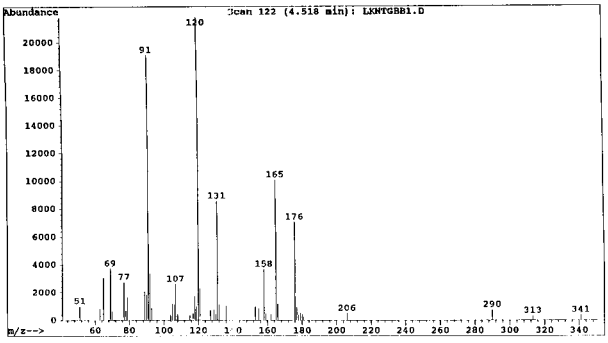


Figure 5 DIP-MS mass spectrum from the NTG and BZMA polymer, electron energy at 70 eV and ion source temperature at 60°C.

Theoretically, the reaction of the vinyl group of the methacrylate monomer with any of these free radical forms of NTG (III, IV, V, VI, VII) is possible. A plausible structure for an intact fragment from the end of the polymer structure that gives rise to the ion at m/z 294 is formed by the addition of the *N*-tolylglycine radical (VI) to the vinyl group of HEMA (Fig. 3). The ion at 277 is due to elimination of OH from the m/z 294 ion. The characteristic ion at m/z 165 was attributed to NTG. The base peak at m/z 120 accounts for the loss of (— COOH) from NTG. The tropylium ion peak at m/z 91 $(C_6H_5CH_2)^{+\bullet}$ is indicative of resonance-stabilized benzyl ion.

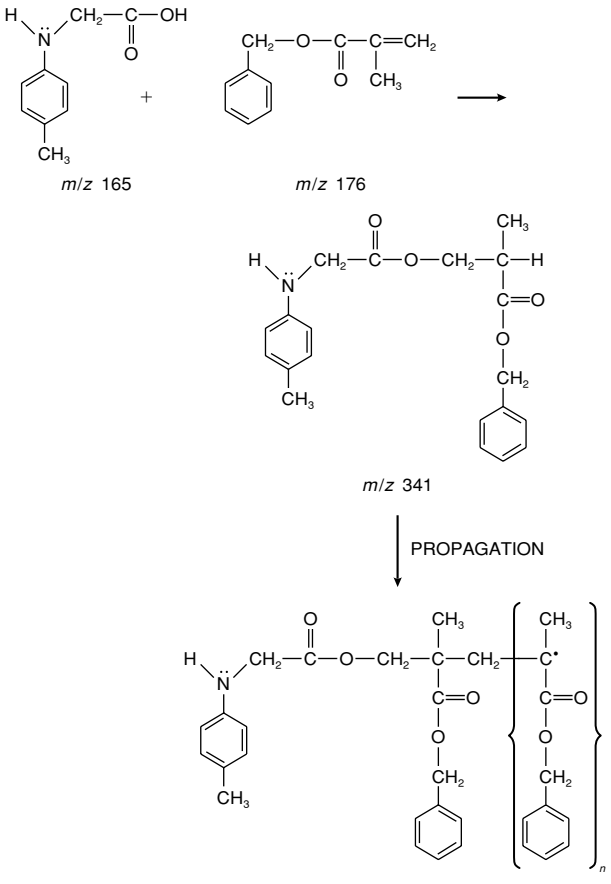
In order to study and observe the formation of the polymers and their products, the samples were taken from the beginning of mixing of NTG and HEMA every 30 min for the first 10 h and then every 24 h for the following 7 days. The result shows that the polymer forms after 4 h. Equation 1 shows the most probable reactions of NTG with HEMA based on the mass spectral results.

In order to characterize the possible structure of the products in equation 1, the polymer was analyzed by GC-MS. Figure 4 shows a mass spectrum which strongly supports the formation of polymer structure in eq. (1). The molecular ion $M^{+\bullet}$ of TMS derivatized sample of NTG+HEMA polymer was observed at m/z 439. The characteristic ion resulting from CH_3 loss $(M\text{-}15)^+$ was observed at m/z 424. The peak at m/e 278 may be due to M—(—COO—C_2H_4—OTMS). The peak

at 188 may be due to the $(CH_3—CH—COO—CH_2—CH_2—OTMS)^+$ fragment. The intense peak at 143 may be due to $—CH_2—COO—CH_2—C(CH_3)—COO—$ fragment (Scheme 2).

The polymer which formed from reaction of BZMA with NTG was analyzed with the electron energy set at 70 eV and the ion source temperature at 60°C. This was the best condition for the analysis of this polymer (Fig. 5). The molecular ion $M^{+\bullet}$ was observed at m/z 341. The ions at m/z 165 and 176 were due to NTG and BZMA, respectively, and the ion at m/z 120 was due to elimination of (—COOH) from the $M^{+\bullet}$ ion of NTG. A likely mechanism for the formation of the adduct of BZMA and NTG (m/z 341) involves the addition of the radical form(s) of NTG (VI) to the vinyl group of BZMA [eq. (2)].

The polymer resulting from the reaction of NTG (2.6%) with MMA (97.4%) yielded the mass spectrum shown in Figure 6. The m/z 265 may be due to the molecular ion of the polymer of (MMA+NTG). The ion at m/z 120 was due to elimination of (—COOH) from NTG.



Equation 2 The mechanism proposed for the formation of molecular ion (M^+ 341), which can arise from the addition of the NTG radicals (VI) to the vinyl group of BZMA.

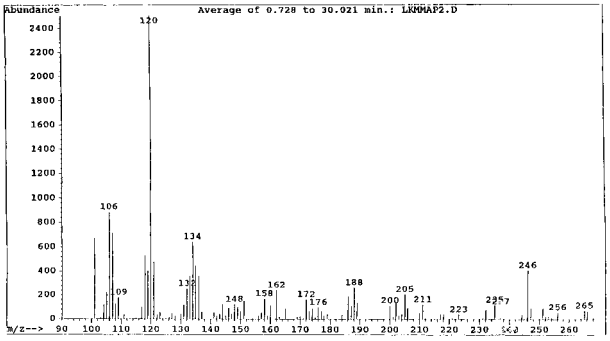


Figure 6 DIP-MS mass spectrum of the reaction product of NTG and MMA. Same conditions as Figure 1.

CONCLUSION

Analysis of acrylic polymers by direct inlet mass spectrometry is a useful analytical technique for the analysis of the end groups of these polymers. In this study this technique demonstrated the presence of *N*-phenylglycine or *N*-tolylglycine in the fragmentation products of the acrylic polymers derived from these *N*-aryl-α-amino acids. Several reaction pathways for forming initiating radicals from these amino acids are possible, and further studies are needed before definitive mechanism(s) can be identified. However, these experiments were quite successful in supporting the hypothesis that the polymer products do indeed posses functional groups derived directly from the NAAAs studied, i.e., NPG and NTG.

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