A GC–MS Study of the Addition Reaction of Aryl Amines with Acrylic Monomers

M. FARAHANI,[1] J. M. ANTONUCCI,[2] L. R. KARAM[3]

[1] ADAHF Paffenbarger Research Center, NIST, Gaithersburg, Maryland 20899

[2] Polymers Division, NIST, Gaithersburg, Maryland 20899

[3] Ionizing Radiation Division, NIST, Gaithersburg, Maryland 20899

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ABSTRACT: Previous studies have shown that the interaction of carboxylic acid groups with the amine functionalities of aryl amines, especially secondary and tertiary aryl amines, can lead to the free-radical polymerization of acrylic monomers such as methyl methacrylate. In this study, the Michael addition reaction of primary and secondary aryl amines with acrylic monomers such as acrylic acid (AA) was investigated. Equivalent amounts of either *p*-toluidine (PT) or *N*-phenylglycine (NPG) and AA were combined in polar solvents such as ethanol. The reactions were conducted at ambient (23°C) or near-ambient (37–60°C) temperatures. Samples (about 3–5 mg) of these products were then trimethylsilylated with a solution consisting of 0.4 mL of bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and 0.4 mL of acetonitrile by heating for 30 min at 140°C under N_2. These derivatives were characterized by gas chromatography–mass spectrometry (GC–MS). The GC–MS analyses suggest that 1 mol of the primary amine PT had reacted with 2 mol of AA to yield the expected *N*-*p*-tolyliminodipropionic acid. Similarly, the secondary amine NPG added to 1 mol of AA yielded the corresponding mixed iminodiacid, *N*-phenyliminoacetic–propionic acid. It would appear that the Michael reaction of primary and secondary amines with acrylic monomers may offer a general, facile synthetic route to a variety of tertiary amines. Aryl amino acids of the type synthesized in this study may find use in a number of dental applications, e.g., as surface-active adhesive agents and as polymerization initiators or activators. J Appl Polym Sci **67:** 1545–1551, 1998

INTRODUCTION

Previously, spontaneous polymerization of a variety of acrylic monomers (e.g., methyl methacrylate and 2-hydroxyethyl methacrylate) was observed after activation with a combination of various carboxylic acids (e.g., 2,4-dichlorobenzoic acid and trifluoroacetic acid) and aromatic amines (e.g., *N*,*N*-dimethylamino-*p*-toluidine, *N*-phenylglycine).[1–3] The mechanism(s) for these polymerizations appeared to involve the intermediacy of an unstable salt or complex that formed because of the interaction of the carboxylic acid and amine functional groups of the reactants, followed by its decomposition into initiating radicals.[1] The same type of complex formation and decomposition probably also accounts for the addition of small amounts of radical species derived from *N*-aryl-α-amino acids such as *N*-phenylglycine to acrylic monomers that cause their subsequent polymerization.[2,3] *N*-Aryl-α-amino acids also can produce free radicals under the oxidative conditions involved in initiating the polymerization of adhesive

Correspondence to: M. Farahani.

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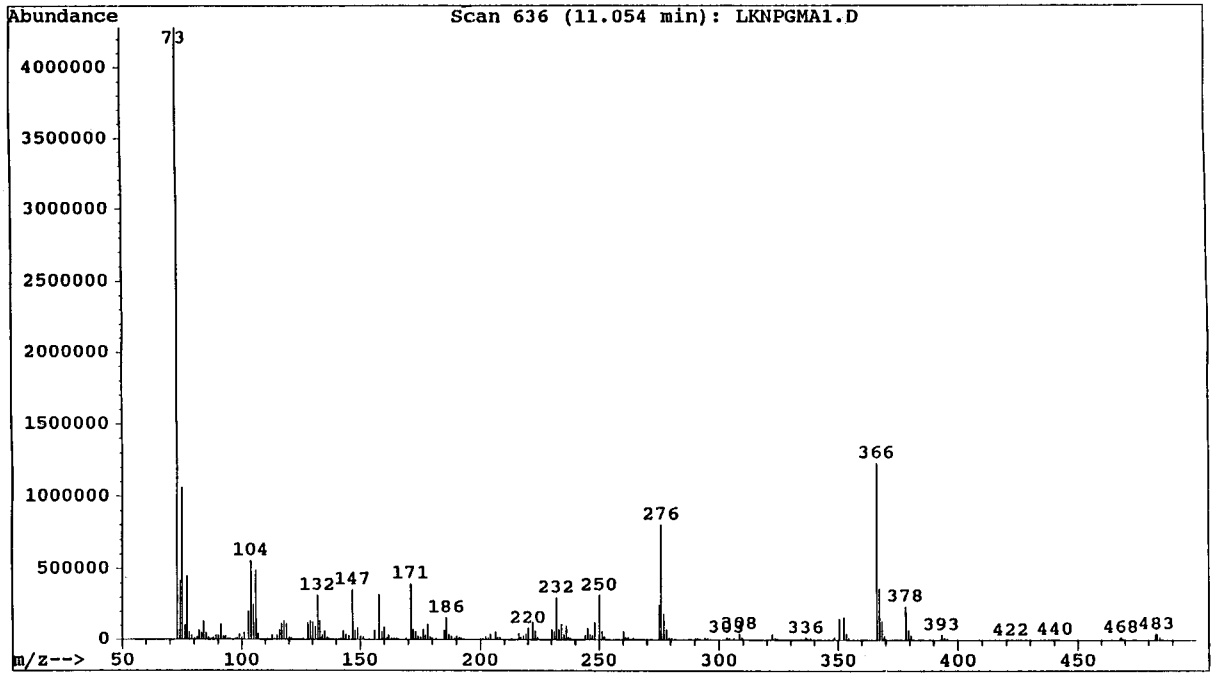


Figure 1 GC–MS mass spectrum of TMS derivative of NPG + MaA.

bonding resins.[4] Finally, it has been reported that free-radical formation occurs by the photosensitized decarboxylation of *N*-phenylglycine in the presence of (thio)xanthene dye.[5]

The goal of this study was to investigate the feasibility of conducting Michael addition reactions with equivalent amounts of either primary or secondary aryl amines and various acrylic or similar monomers and, thereby, provide a facile synthesis of a wide range of aryl tertiary amines. The successful Michael addition reaction of primary or secondary amines to acrylic monomers would thus offer a general, convenient route to a variety of potential adhesive agents and polymerization initiators or activators. In addition, this study can provide further insight into the mechanisms of how these aryl amines interact with acrylic monomers. In this study, gas chromatography–mass spectrometry (GC–MS) was used to characterize the reaction products.

EXPERIMENTAL*

N-Phenylglycine (NPG), *p*-toluidine (PT), acrylic acid (AA), maleic acid (MaA), itaconic acid (ITA), and vinyl phosphonic acid (VPA) were used as received from Aldrich Chemical Co. Bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and acetonitrile were used as received from Pierce.

General Procedure for Michael Addition Reaction

Equal molar quantities of the amine and the vinyl monomer were dissolved in pure ethanol in a flask. The reactions were conducted with magnetic stirring at 23°C for 24 h prior to removal of the solvent and any unreacted, volatile monomers by rotary evaporation. It also was possible to conduct these reactions at elevated temperatures, e.g., 37–65°C. In all these reactions, there was virtually no evidence of polymeric products as was the case in previous studies that used small quantities of NPG with acrylic monomers.[2,3]

Trimethylsilylation

Samples of NPG, PT, ITA, VPA, and the reaction products of NPG (0.01 mol) + AA (0.01 mol), PT (0.01 mol) + AA (0.02 mol), NPG (0.01 mol) + MaA (0.01 mol), NPG (0.01 mol) + ITA (0.01 mol), and NPG (2×10^{-4} mol) + VPA (2×10^{-4} mol) were trimethylsilylated in Teflon-capped hypovials with 0.4 mL each of BSTFA and acetonitrile (volume ratio 1 : 1) by heating for 30 min at 140°C. (Reactant amounts were measured on a

* Certain commercial materials and equipment are identified in this article 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.

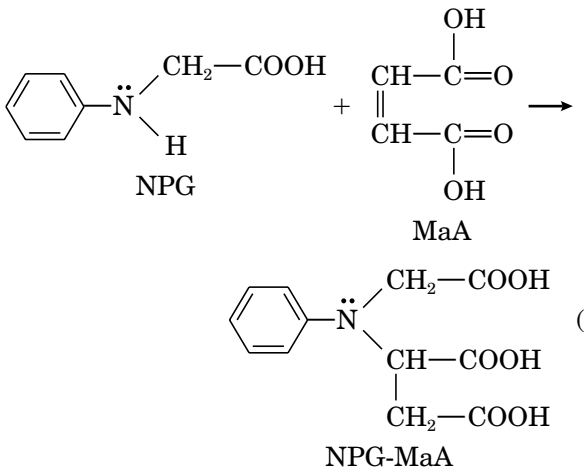
mass basis except for the derivatization reagent and solvent.)

Gas Chromatography–Mass Spectrometry (GC–MS)

A Hewlett-Packard Model 5890 series gas chromatograph equipped 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, 30–90 s split). Detection was done with an HP 5970 mass selective detector (50–800 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

AA, MaA, ITA, VPA, PT, and NPG were analyzed by GC–MS separately under the same experimental conditions as were their Michael addition products. The reaction products of *N*-phenylglycine with maleic acid were analyzed by GC–MS. Figure 1 shows a mass spectrum obtained from NPG + MaA after trimethylsilylation (TMS). The molecular ion $M^{+\bullet}$ of a TMS derivatized sample of NPG–MaA was observed at m/z 483. The characteristic ion resulting from CH_3 loss $(M\text{-}15)^+$ was observed at m/z 468. The intense peak at m/z 366 was due to (M-COOTMS: 117). The characteristic ion at 378 was due to the elimination of (OOTMS: 105) from $M^{+\bullet}$. Peaks at 223 and m/z 260 are due to NPG and MaA after TMS, respectively. The ions at m/z 73 and 147 are commonly observed with TMS derivatives. From these data, this mass spectrum was attributed to the following addition compound derived from the Michael addition reaction [eq. (1)]:



(1)

This compound, *N*-phenyliminoacetic–succinic acid (NPG–MaA), is formed by the reaction of NPG across the double bond of maleic acid.

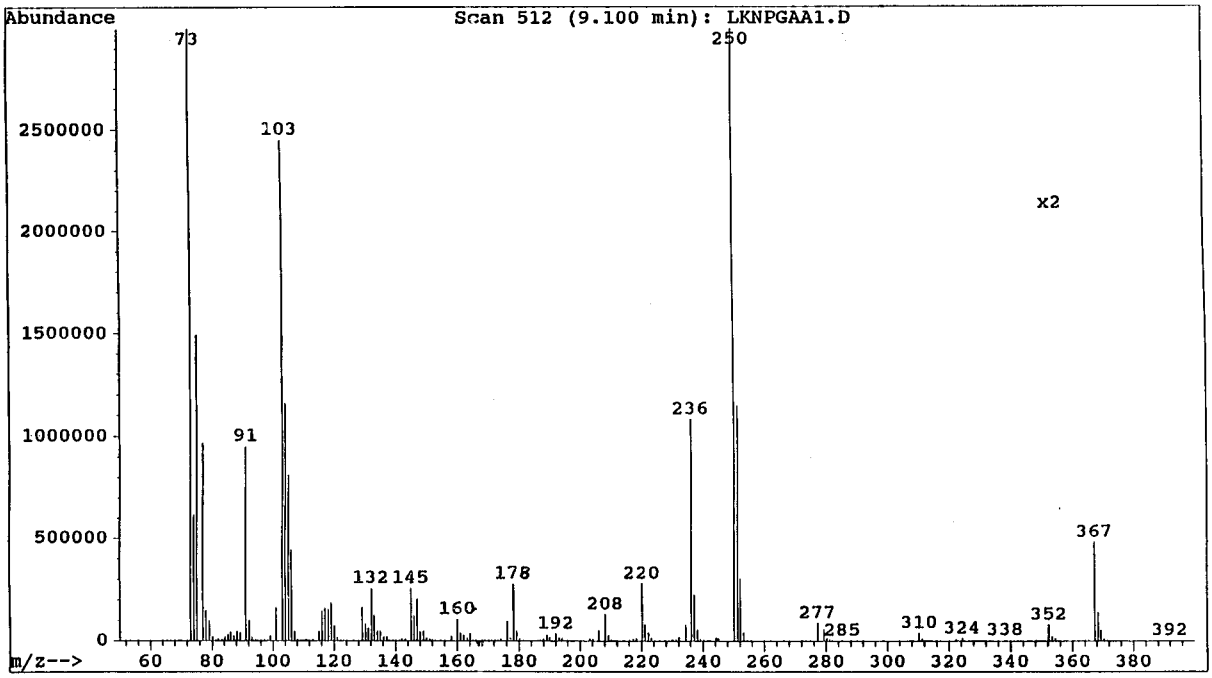
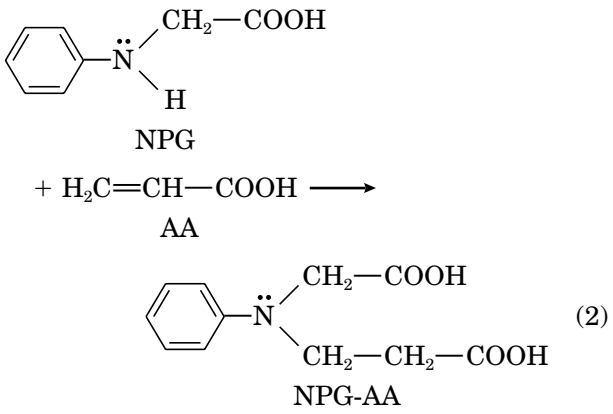


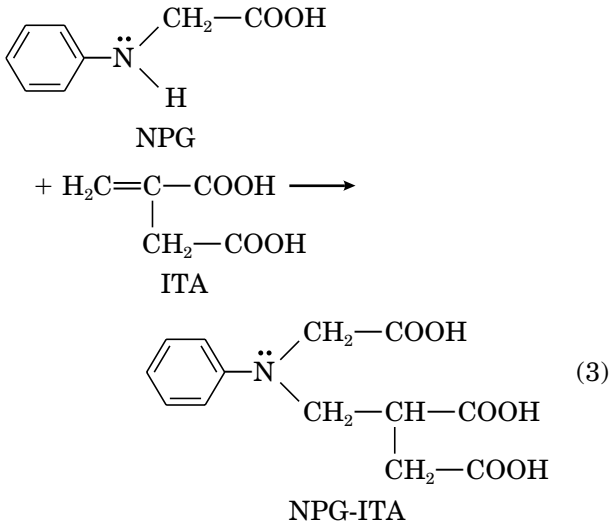
Figure 2 GC–MS mass spectrum of TMS derivative of NPG + AA.

The reaction product of NPG with AA was similarly analyzed by GC–MS. Figure 2 shows a mass spectrum obtained from NPG + AA after trimethylsilylation. The molecular ion $M^{+\bullet}$ and a characteristic $(M—CH_3)^+$ ion were observed at m/z 367 and 352, respectively. In the displayed spectrum, the ion at m/z 277 was due to the elimination of (HOTMS: 90) from the $M^{+\bullet}$ ion, and the ion at m/z 250, due to elimination of (COOTMS: 117) from the $M^{+\bullet}$ ion. Loss of (CH_2—COOTMS: 131) from $M^{+\bullet}$ accounted for the ion at m/z 236. The peaks at 223 and m/z 144 are due to NPG and AA after TMS, respectively. From this mass spectrum, the product was assigned the simple 1 : 1 adduct structure, NPG–AA [eq. (2)]:



(2)

The reaction product of NPG with ITA was analyzed by GC–MS. Figure 3 shows a mass spectrum obtained from the product of the reaction of NPG + ITA after trimethylsilylation. The molecular ion $M^{+\bullet}$ and characteristic $(M—CH_3)^+$ ions were observed at m/z 497 and 482, respectively. The peak at 223 was NPG after TMS, respectively [eq. (3)]:



(3)

The reaction product of NPG with VPA also was analyzed by GC–MS. Figure 4 shows a mass spectrum obtained from the product of the NPG + VPA

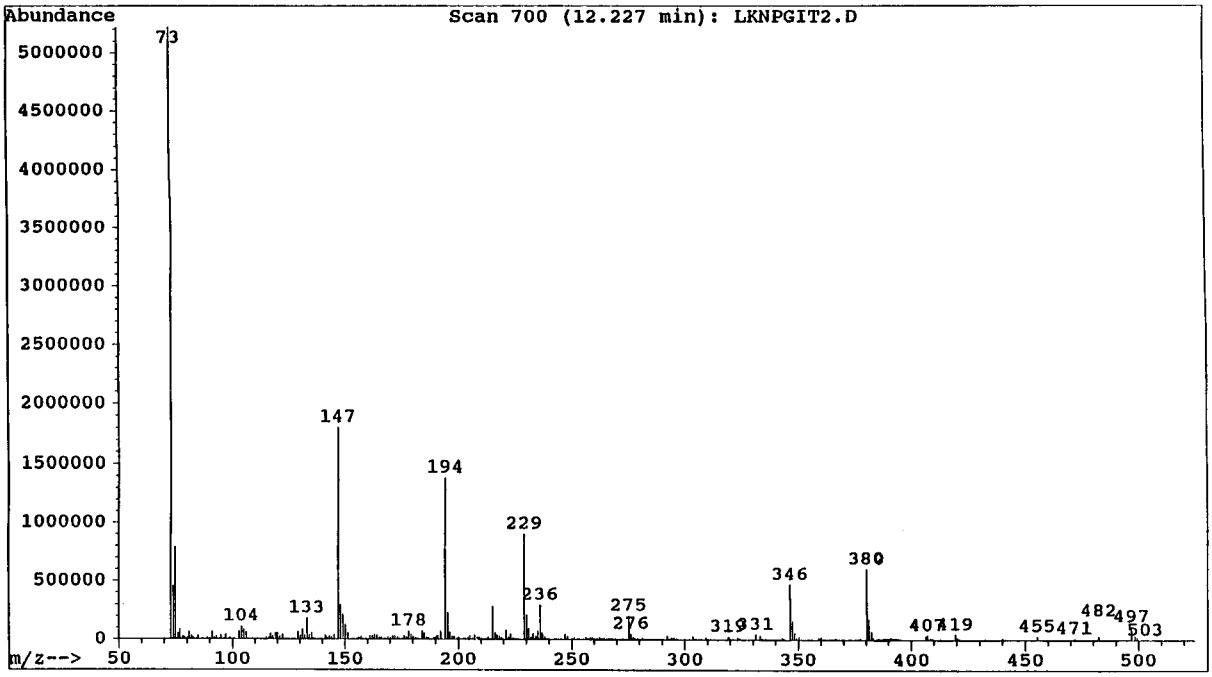


Figure 3 GC–MS mass spectrum of TMS derivative of NPG + ITA.

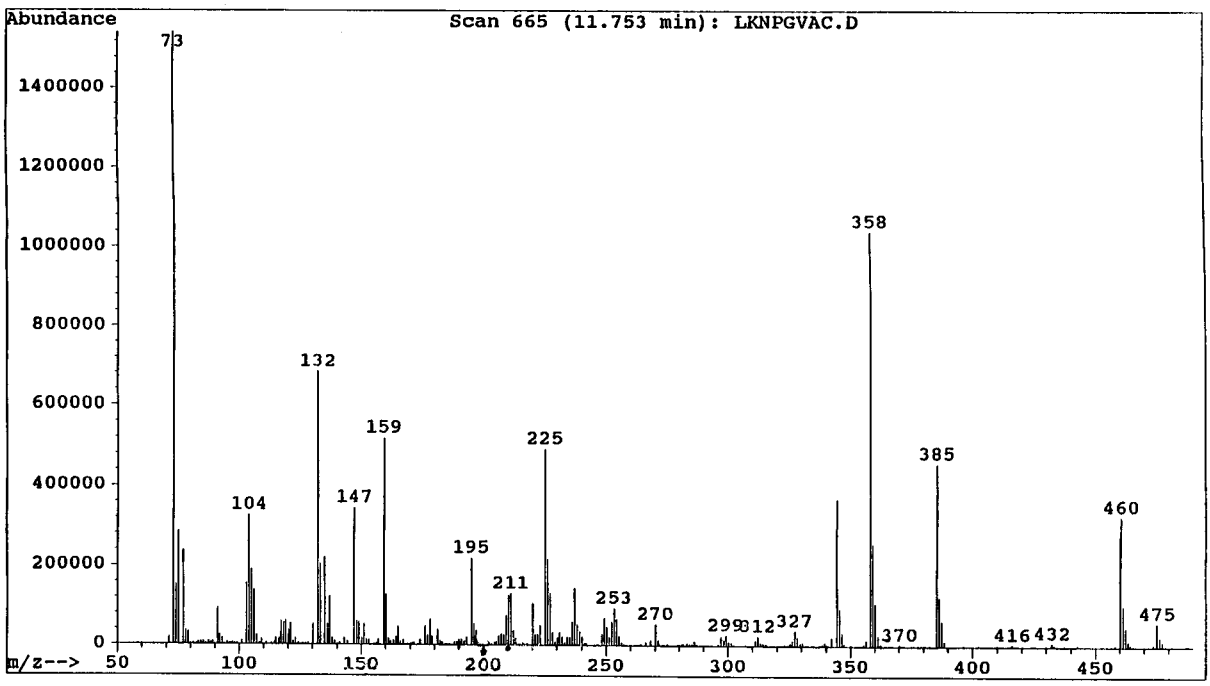
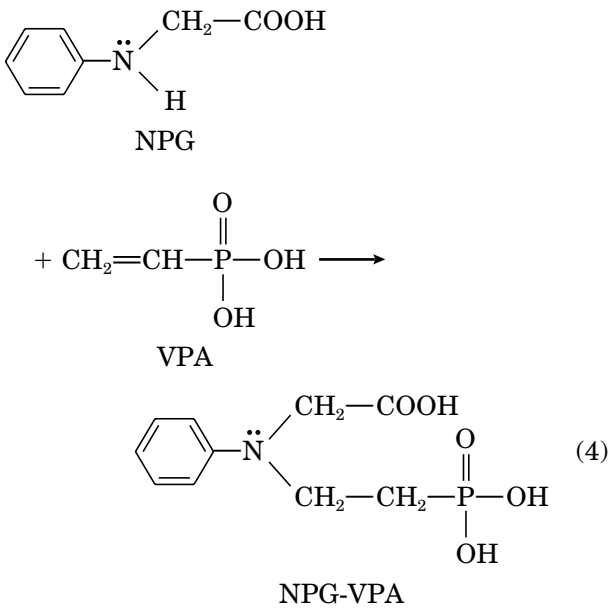
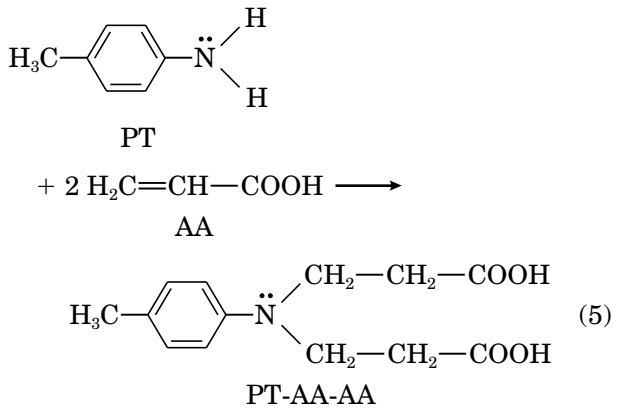


Figure 4 GC–MS mass spectrum of TMS derivative of NPG + VPA.

reaction after trimethylsilylation. The molecular ion $M^{+\bullet}$ and characteristic $(M—CH_3)^+$ ions were observed at *m/z* 475 and 460, respectively. In the displayed spectrum, the ion at *m/z* 385 was due to the elimination of (HOTMS: 90) from the $M^{+\bullet}$ ion, and the ion at *m/z* 358, to the elimination of (COOTMS: 117) from the $M^{+\bullet}$ ion. Loss of (CH_2—COOTMS: 131) from $M^{+\bullet}$ accounted for the ion at *m/z* 344. Peaks at 223 and *m/z* 252 are due to NPG and VPA after TMS, respectively. [eq. (4)]:



By the same GC–MS method, the reaction product of the primary aryl amine, *p*-toluidine (PT) with acrylic acid (AA) was analyzed. Figure 5 shows the mass spectrum obtained from the PT + AA reaction product after trimethylsilylation. The molecular ion $M^{+\bullet}$ was observed at *m/z* 395. Loss of (CH_2—COOTMS: 131) from $M^{+\bullet}$ accounted for the ion at *m/z* 264. The peaks at 251 and *m/z* 144 are due to PT and AA after TMS, respectively. From this mass spectrum, the reaction product appears to result from a two-stage Michael addition reaction involving the reaction of PT with two molecules of AA [eq. (5)]:



The mass spectrum also showed the possibility of the reaction of one molecule of PT with three

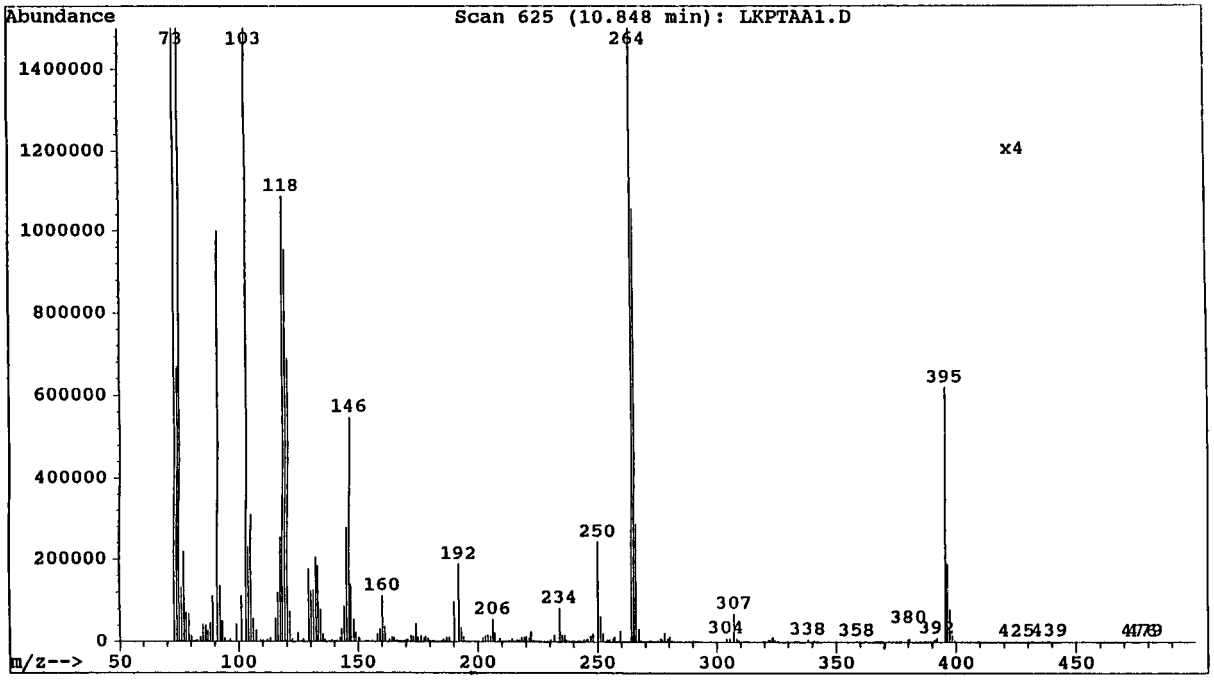


Figure 5 GC–MS mass spectrum of TMS derivative of PT + AA.

molecules of AA: The molecular ion $M^{+\bullet}$ and characteristic $(M—CH_3)^+$ ions were observed at m/z 539 and 524 after TMS, respectively (Fig. 6). The ion at m/z 422 was due to the elimination of (COOTMS: 117) from the $M^{+\bullet}$ ion. Loss of (CH_2—COOTMS: 131) from the $M^{+\bullet}$ accounted for the ion at m/z 408. The small peaks at 251 and m/z 144 are due to residual PT and AA as

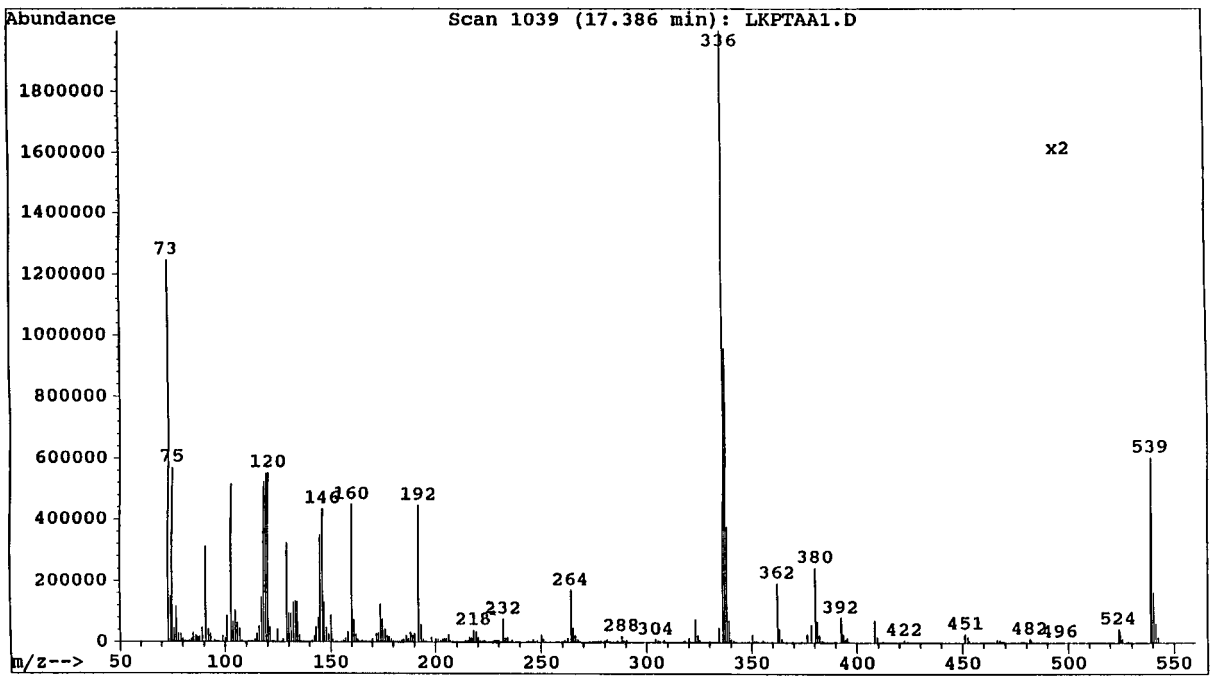
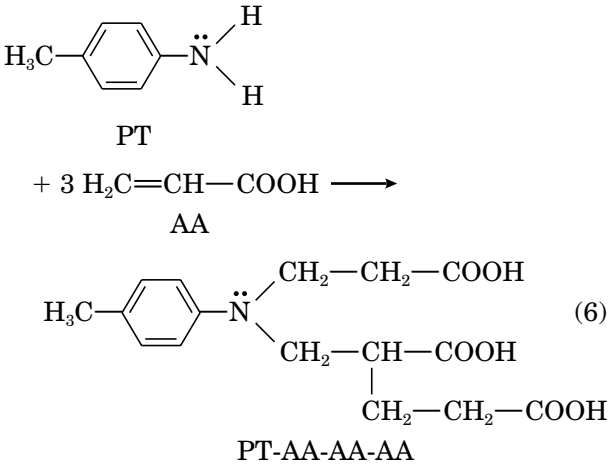


Figure 6 GC–MS mass spectrum of TMS derivative of PT + 3AA.

before. From these results, it is hypothesized that this product, PT–$(AA)_3$, arises from the reaction of one molecule of PT with three molecules of AA [eq. (6)]:



(6)

Under the reaction conditions employed, there was no evidence for the formation of the simple 1 : 1 adduct from PT and AA. Further studies are planned that will use infrared and nuclear magnetic spectroscopies as well as GC–MS to characterize the products of these interesting reactions.

CONCLUSION

It has been shown by GC–MS that by controlling the stoichiometry of the reagents the Michael reaction of primary and secondary aryl amines with acrylic and vinyl monomers is favored over polymerization. The Michael reaction of primary and secondary amines with acrylic monomers offers a general, facile synthesis of many tertiary amines. These tertiary amines may find use in a number of dental applications, e.g., as surface-active adhesive agents and as polymerization initiators or activators.

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