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CHEMICAL CONVERSION OF ENERGETIC MATERIALS TO HIGHER VALUE PRODUCTS*

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Abstract

The objective of this program is to develop novel, innovative solutions for the disposal of surplus explosives resulting from the demilitarization of nuclear and conventional munitions. Studies related to the conversion of TNT and Explosive D to potentially useful materials are described.

Introduction

The demilitarization of nuclear and conventional munitions is producing millions of pounds of surplus explosives (energetic materials).[1] Historically, surplus explosives have been disposed of by open burning/open detonation (OB/OD). The disposal of these materials by OB/OD is becoming unacceptable due to public concerns and increasingly stringent environmental regulations. In addition, the presence of such a large inventory of militarily useful explosives increases proliferation risks. Environmentally sound and cost-effective alternatives to OB/OD are needed. We are investigating the chemical conversion of energetic materials to higher value products.[2] This paper describes efforts at Lawrence Livermore National Laboratory (LLNL) and elsewhere to use TNT, Explosive D (ammonium picrate) and other surplus munitions as starting materials for the synthesis of higher value products (Figure 1).

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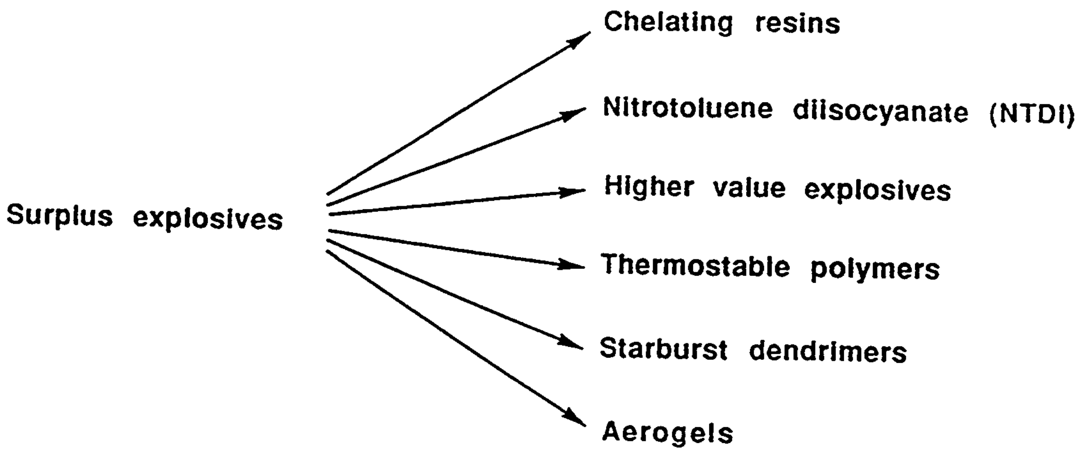

Figure 1. Use of surplus explosives as chemical feedstocks for higher value products.

Chemical Conversions of TNT

There are many references in the chemical literature describing the conversion of TNT to other molecules. For example, the reduction of TNT to aminodinitrotoluenes[3], diaminonitrotoluenes[4] and triaminotoluene[5] is well known. The catalytic hydrogenation of TNT to 2,4,6-triaminotoluene (TAT) and the use of TAT to prepare monomers for the production of novel polymers has been reported.[6] A. L. Rusanov and co-workers have investigated the use of TNT to prepare thermostable polymers.[7] TNT was converted into 3,5-diaminoanisole which was reacted with dianhydrides of aromatic tetracarboxylic acids to prepare a number of aromatic polyimides.

Phloroglucinol is used in the pharmaceutical, cosmetics, textile-dying and photographic industries. The commercial conversion of TNT to phloroglucinol is shown in Figure 2.[8] TNT is oxidized by dichromate in sulfuric acid to give

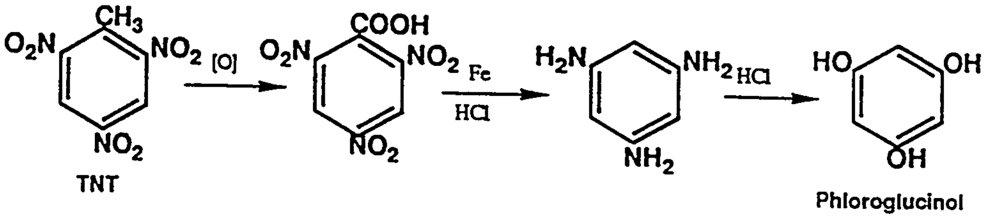

Figure 2. Conversion of TNT to phloroglucinol.

2,4,6-trinitrobenzoic acid which is then treated with iron and hydrochloric acid to allow reduction of the nitro groups and simultaneous decarboxylation to give 1,3,5-triaminobenzene. Acid hydrolysis (108° C) of the 1,3,5-triaminobenzene yields phloroglucinol. The use of this process was discontinued in the USA in the 1970s due to problems associated with the waste disposal of acid liquors, iron, chromium and ammonium salts.[9] Conversions of TNT to precursors we have found useful in our studies are shown in Figure 3.

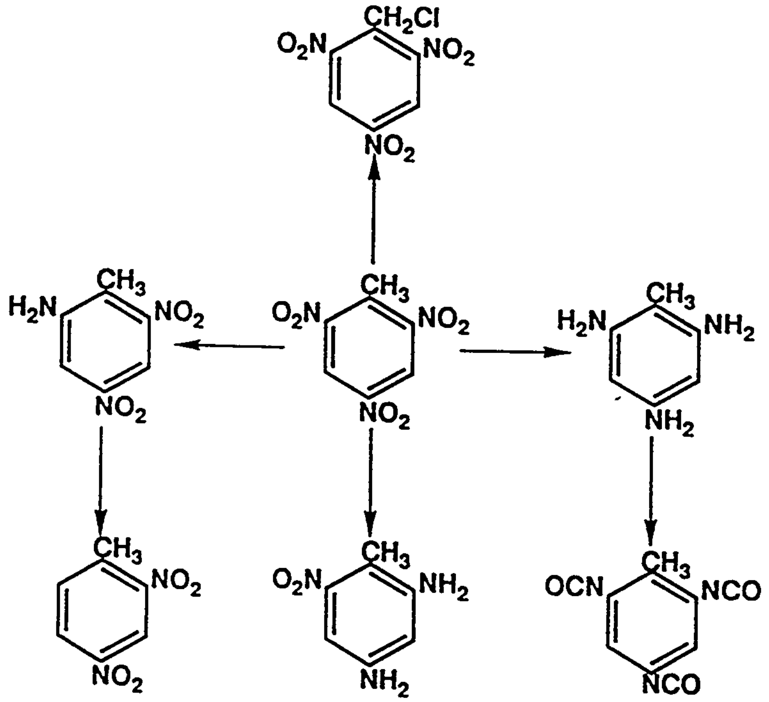

Figure 3. Conversion of TNT to useful precursors.

Conversion of TNT to TATB

The conversion of TNT to TATB was originally described by R. L. Atkins[10] and is illustrated in Figure 4. The ammonolysis of pentanitroaniline (PNA) yields TATB contaminated with polynitrophenol by-products (R. Atkins, personal communication). We are seeking to improve the production of TATB from TNT with respect to waste minimization and increased purity. The recent work of M. F. Foltz (LLNL) in preparing 100-2000 µm crystalline TATB[11] should facilitate our process development studies.

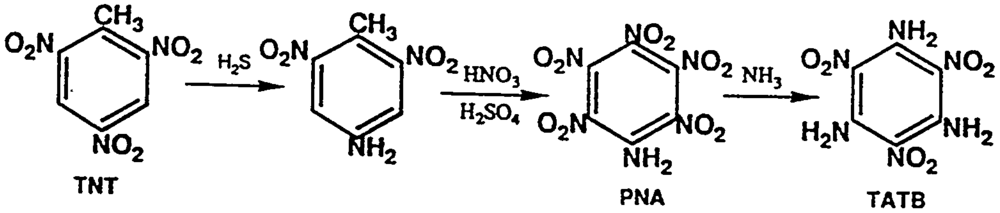

Figure 4. Conversion of TNT to TATB.

Conversion of TNT to DATNT

Iyer has shown that the TNT molecule is significantly desensitized by substitution of ring hydrogens by $-NH_2$ groups.[12] 3,5-Diamino-2,4,6-trinitrotoluene (DATNT) is less impact-sensitive than TNT. The CJ pressure and detonation velocity calculated for DATNT indicate that it should be a more powerful explosive than TNT. The presently available syntheses of DATNT require relatively harsh reaction conditions and utilize starting materials that are either expensive or commercially unavailable.[12,13]

The direct amination of nitroarenes by vicarious nucleophilic substitution (VNS) of hydrogen was first reported by Meisenheimer and Patzig who described the reaction of hydroxylamine with 1,3-dinitrobenzene to yield 2,4-dinitro-1,3-phenylenediamine.[14] The use of 4-amino-1,2,4-triazole[15] and various sulfenamides[15] as aminating agents in VNS reactions has been reported. We have directly converted TNT to DATNT using VNS reactions (Figure 5). The use of VNS reactions to prepare other energetic materials is under investigation.

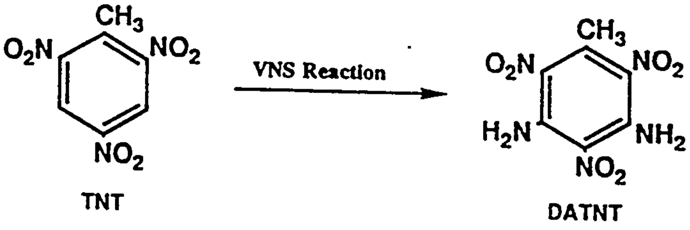

Figure 5. Conversion of TNT to DATNT by direct amination.

Conversion of TNT to TDI and NTDI

Tolylene 2,4-diisocyanate (TDI) is the basic raw material for production of polyurethane foams. It is produced in a reaction sequence where toluene is dinitrated, the 2,4-dinitrotoluene hydrogenated to yield 2,4-diaminotoluene, which in turn is treated with phosgene to yield TDI. In a similar fashion TNT can be reduced to 2,4-diamino-6-nitrotoluene and then converted to nitrotolylene diisocyanate (NTDI). The production of TDI and NTDI from toluene or TNT is illustrated in Figure 6.

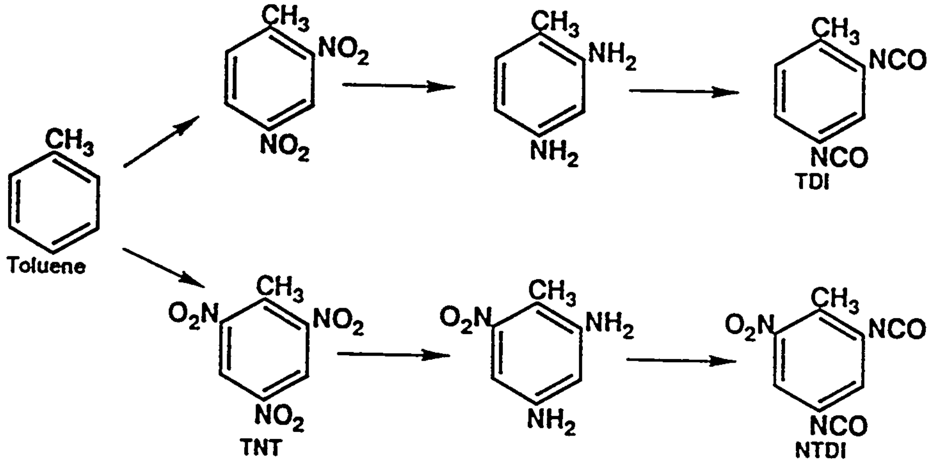

Figure 6. Preparation of TDI and NTDI.

The preparation and characterization of NTDI as a component in the production of polyurethanes and related polymers is under investigation. The presence of the nitro group is expected to make NTDI a more reactive diisocyanate than TDI. This should allow for the production of very rapidly curing urethanes without the need for accelerating catalysts. The high reactivity rates of NTDI systems are expected to find application in reaction injection molding where a catalyst must currently be used to achieve short cycle times.

Chelating Resins Derived from Trinitroarenes

The aminopolycarboxylic acids are highly effective chelating ligands.[17] They are essentially derived from aminoacetic acid (glycine) and related derivatives such as iminodiacetic acid (IDA). The covalent binding of IDA to copolymers of styrene-divinylbenzene provides the basis for commercially available chelating ion exchange resins. These resins show unusually high selectivity for copper, iron and other heavy metals and have been employed in the removal of heavy metals from industrial waste streams. Unfortunately, carcinogenic chloromethyl methyl ether (CMME)[18] is required for the preparation of commercial chelating resins that incorporate polystyrene and IDA. The report of a chelating resin which incorporated a tetracarboxymethyl derivative of 3-phenylenediamine[19] suggested the possibility of preparing related materials by grafting trinitroarene-derived precursors onto copolymers of styrene-divinylbenzene.

The general approach we are using (Figure 7) derives from strategies originally developed for the preparation of improved resin supports for solid phase peptide synthesis.[20,21] Pathway 1 shows the reduction of a trinitroarene to the corresponding triaminoarene followed by complete carboxymethylation prior to the incorporation (grafting) of the (IDA)3 -arene derivative onto the copolymer of styrene-divinylbenzene. Pathway 2 features the incorporation (grafting) of the

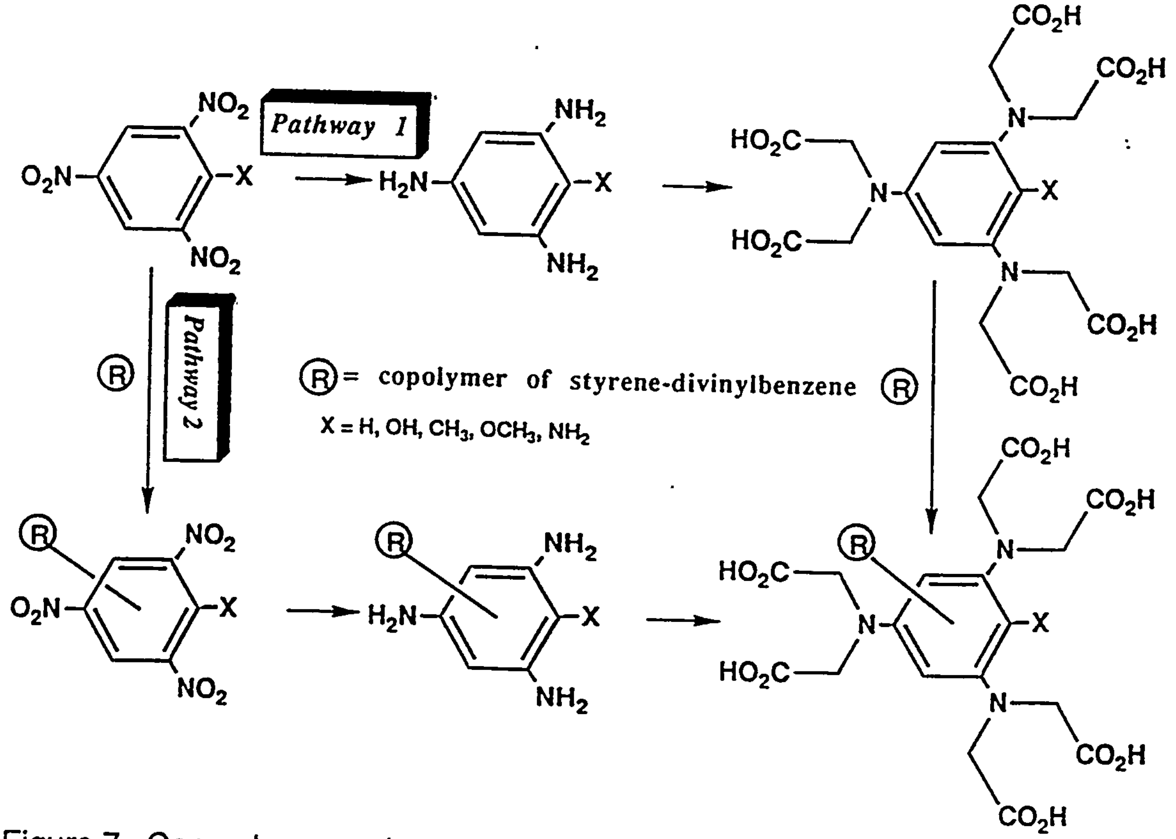

Figure 7. General approach to chelating resins from trinitroarenes.

trinitroarene onto the styrene-divinylbenzene support prior to the reduction and carboxymethylation reactions. The Tscherniac-Einhorn reaction[20,21] was modified to allow the amidoalkylation of polystyrene by a variety of amide and carbamate derivatives. Thus, N-picrylacetamide reacts with paraformaldehyde, trifluoromethanesulfonic acid and a copolymer of styrene-divinylbenzene in refluxing ethylene dichloride to give the desired amidoalkylation product at modest substitution levels. Acid hydrolysis of this product provides picryl-aminomethyl-polystyrene.

Pathway 2 (Figure 7) was originally thought to be the more accessible route to the target resin. Limitations have been found in the reduction step, however. We have confirmed that although phenylhydrazine[22] is the reagent of choice for smoothly reducing polynitroarenes to polyaminoarenes, it favors cleavage rather than reduction of both the dinitrophenyl and trinitrophenyl derivatives of aminomethyl-polystyrene (Figure 8). This finding indicates that pathway 1 (Figure 7) will be the preferred route for the conversion of trinitroarenes and related compounds to chelating resins.

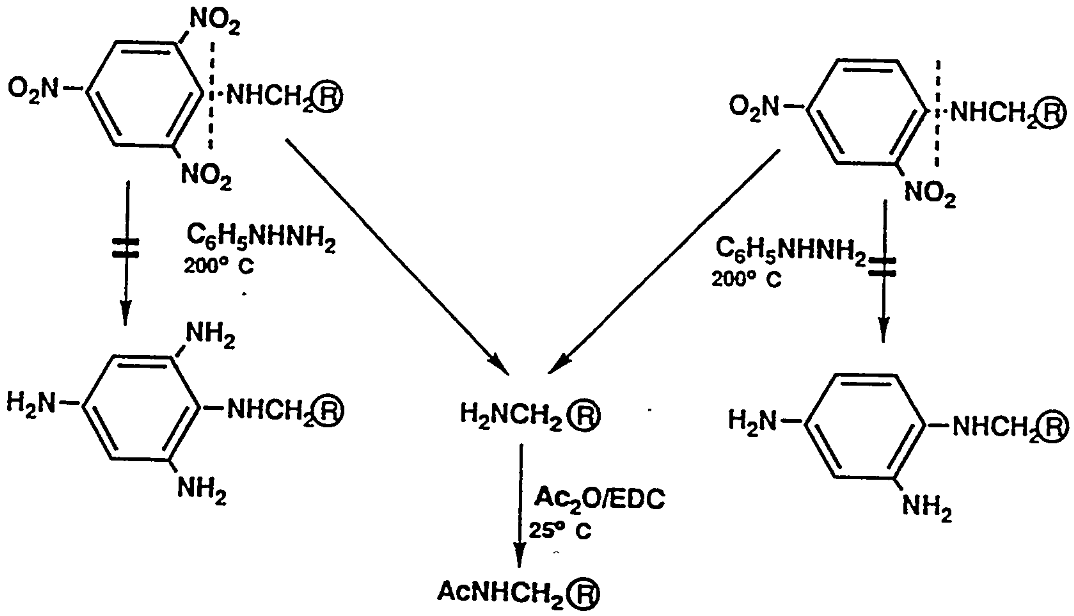

Figure 8. Reduction of nitroarylaminomethylpolystyrene resins with phenylhydrazine.

Summary and Conclusions

The disposal of surplus explosives obtained from the demilitarization of nuclear and conventional weapons is a large and ever-growing problem with global consequences. Formerly acceptable and inexpensive destruction technologies (OB/OD) are losing acceptance due to environmental concerns. The chemical conversion of energetic materials to higher value products represents a win-win situation. Liabilities (surplus explosives) are converted to assets (useful products) and the environment is spared the burden of presently available destruction technologies.

References

1. C. O. Pruneda, A. R. Mitchell and J. Humphrey, "Reusing the High Explosives from Dismantled Nuclear Weapons," *Energy and Technology Review*, LLNL, Livermore, CA, UCRL-52000-93-11·12 (1993), p.19.

2. A. R. Mitchell and R. D. Sanner, "Chemical Conversion of Energetic Materials to Higher Value Products," in *Energetic Materials- Insensitivity and Environmental Awareness, Proc. 24th Intl. Annual Conference of ICT*, H. Ebeling, Ed., Karlsruhe, Germany, 1993, p. 38.

3. A. T. Nielsen, R. A. Henry, W. P. Norris, R. L. Atkins, D. W. Moore, A. H. Lepie, C. L. Coon, R. J. Spanggord and D. V. H. Son, "Synthetic Routes to Aminodinitrotoluenes," *J. Org. Chem.*, **44**, 2499 (1979).

4. E. W. Lowe, *Selective Reduction of Polynitro Aromatics*, U. S. Patent No. 2,669,584 (1950).

5. J. E. Gill, R. MacGillivray and J. Munro, "The Preparation of Symmetrical Aromatic Triamines and Triisocyanates," *J. Chem. Soc.*, 1753 (1949).

6. M. Lübben, H. Scholles, K. Reichelt and K.-H. Kluger, "Verwertung von TNT durch Hydrieren," in *Waste Management of Energetic Materials and Polymers, Proc. 23rd Intl. Conference of ICT*, H. H. Krause, Ed., Karlsruhe, Germany, 1992, p. 8.

7. A. L. Rusanov, L. G. Komarova, A. M. Trushkin, S. A. Shevelev, M. D. Dutov, O. V. Serushkina and A. M. Andrievskii, "3,5-Diaminoanisole-Based Polyimides," *Vysokomol. Soedin.,Ser. B*, **35**, 883 (1993).

8. M.L. Kastens and J.F. Kaplan, "TNT into Phloroglucinol," *Ind. Eng. News*, **42**, 402 (1950).

9. H. Dressler and S. N. Holter, "(Polyhydroxy)benzenes," in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., H.F. Mark, D.F. Othmer, C.G. Overberger and G.T. Seaborg, Eds., Wiley, New York, 1982, p. 670.

10. R. L. Atkins, A.T.Nielsen and W.P.Norris, *New Method for Preparing Pentanitroaniline and Triaminotrinitrobenzenes from Trinitrotoluene*, U. S. Patent No. 4,248,798 (1981).

11. M. F. Foltz, D. L. Ornellas, P. F. Pagoria and A. R. Mitchell, "Recrystallization and Solubility of 1,3,5-Triamino-2,4,6-trinitrobenzene in Dimethyl Sulfoxide," *J. Mater. Sci.*, **31**, 1893 (1996).

12. S. Iyer, "Explosive Desensitization Studies Via Chemical Group Modification. II. 3,5-Diamino- and 3,5-Dichloro-2,4,6-Trinitrotoluene," *J. Energetic Materials*, **2**, 151 (1984).

13. A. P. Marchand and G. M. Reddy, "Improved Synthesis of 3,5-Diamino-2,4,6-trinitrotoluene," *Synthesis*, 261 (1992).

14. J. Meisenheimer and E. Patzig, "Directe Einführung von Aminogruppen in den Kern aromatischer Körper", *Ber.*, **39**, 2533 (1906).

15. A. R. Katritzky and K. S. Laurenzo, "Direct Amination of Nitrobenzenes by Vicarious Nucleophilic Substitution," *J. Org. Chem.*, **51**, 5039 (1986).

16. M. Makosza and M. Bialecki, "Amination of Nitroarenes with Sulfenamides via Vicarious Nucleophilic Substitution of Hydrogen," *J. Org. Chem.*, **57**, 4784 (1992).

17. C. F. Bell, *Principles and Applications of Metal Chelation* ,Clarendon Press, Oxford, 1977.

18. Occupational Safety and Health Administration, U.S. Department of Labor, *Federal Register*, **39**, 3756 (1974).

19. E. Blasius and G. Oldbrich, "Komplexon-Austauscherharze, Herstellung und analytische Verwendung," *Z. Anal. Chem.*, **151**, 81 (1956).

20. A. R. Mitchell, S. B. H. Kent, B. W. Erickson and R. B. Merrifield, "Preparation of Aminomethyl-polystyrene Resin by Direct Amidomethylation," *Tetrahedron Lett.*, p. 3795 (1976).

21. A. R. Mitchell, S. B. H. Kent, M. Engelhard and R. B. Merrifield, "A New Synthetic Route to BOC-Aminoacyl-4-(oxymethyl)phenylacetamidomethyl-Resin, an Improved Support for Solid Phase Peptide Synthesis," *J. Org. Chem.*, **43**, 2845 (1978).

22. H. Seliger, "Ein neuer Weg zur Synthese von Polstyrol und Styrol-Copolymeren mit primaren aromatischen Aminogruppen," *Makromol. Chem.*, **169**, 83 (1973).