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Functionalized materials from elastomers to high performance thermoplastics

by

Laura Ann Salazar

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Program of Study Committee:
Valerie Sheares Ashby, Major Professor
Richard Larock
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Laura Ann Salazar

has met the dissertation requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program

This dissertation is dedicated to my father,

Dr. David W. Rusch, with love.

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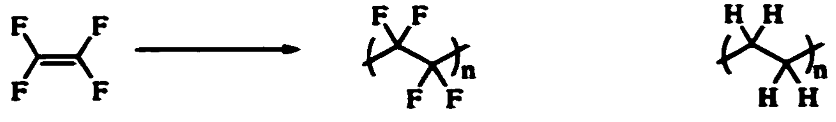
CHAPTER 1. GENERAL INTRODUCTION

Introduction

Synthesis and incorporation of functionalized materials continues to generate significant research interest in academia and in industry. If chosen correctly, a functional group when incorporated into a polymer can deliver enhanced properties, such as adhesion, water solubility, thermal stability, etc. The utility of these new materials has been demonstrated in drug-delivery systems, coatings, membranes and compatibilizers.[1]

Two approaches exist to functionalize a material. The desired moiety can be added to the monomer either before or after polymerization. The polymers used range from low glass transition temperature elastomers to high glass transition temperature, high performance materials. One industrial example of the first approach is the synthesis of Teflon®. Poly(tetrafluoroethylene) (PTFE or Teflon®) is synthesized from tetrafluoroethylene, a functionalized monomer (**Figure 1.1-A**). The resulting material has significant property differences from the parent, poly(ethylene) (**Figure 1.1-B**). Due to the fluorine in the polymer, PTFE has excellent solvent and heat resistance, a low surface energy and a low coefficient of friction.[2] This allows the material to be used in high temperature applications where the surface needs to be nonabrasive and nonstick. This material has a wide spread use in the cooking industry because it allows for ease of cooking and cleaning as a nonstick coating on cookware.



Tetrafluoroethylene A B

Figure 1.1. Poly(tetrafluoroethylene) (A) and poly(ethylene) (B).

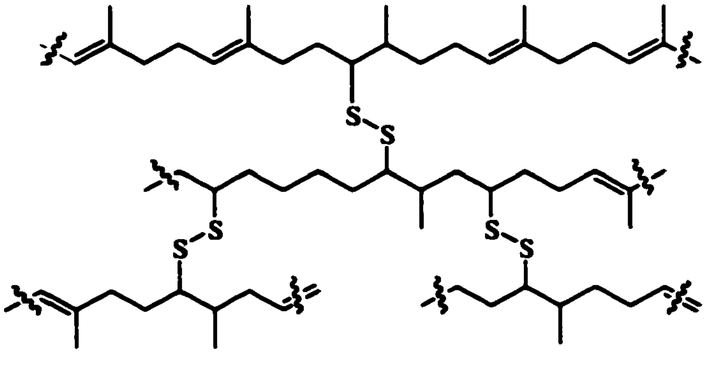


Figure 1.2. Vulcanized rubber by Goodyear.

One of the best examples of the second approach, functionalization after polymerization, is the vulcanization process used to make tires. Natural rubber (from the *Hevea brasiliensis*) has a very low glass transition temperature, is very tacky and would not be useful to make tires without synthetic alteration. Goodyear's invention was the vulcanization of polyisoprene by crosslinking the material with sulfur to create a rubber that was tough enough to withstand the elements of weather and road conditions (**Figure 1.2**).[2] Due to the development of polymerization techniques to make *cis*-polyisoprene, natural rubber is no longer needed for the manufacturing of tires, but vulcanization is still utilized.[2]

Functionalized monomer approach. Using the functionalized monomer approach to create new materials has many advantages in chain growth polymerization. It allows for control over the distribution of the chosen moiety along the polymer backbone, as well as the incorporation of a functionalized monomer into industrial processes and materials. For example, over 60 million pounds of styrene butadiene rubber (SBR) are produced each year.[2] In the case of SBR, the only alteration that can be made is the amount and distribution of the two monomers. SBR could be altered simply by adding a functional group onto either styrene or butadiene to give the material additional properties. This allows for lower incorporation costs industrially because it does not require new processes or equipment for the production of improved materials.

Although the incorporation of functionalized styrene-based monomers has been significantly investigated,[3-6] there has been much less done in the area of functionalized 1,3-butadienes. This is presumably due to the difficult chemistry required to synthesize these diene-based monomers. The first groups attached to 1,3-butadiene were silyl groups due to their versatility and ease of synthesis.[7-10] From there, many other moieties have been investigated for their use with diene-based materials. These include ethers,[11] nitriles,[12,13] esters[14] and amines.[15-25]

The structure of many silyl monomers containing side chains ranging from alkyl silyl to dialkylamino silyl are shown in **Figure 1.3**. Weber investigated 2-trimethylsilyl-1,3-butadiene (**Figure 1.3-A**) and achieved high molecular weights, but also saw broad polydispersities.[7] Free radical polymerizations of 2-trimethylsiloxy-1,3-butadiene (**Figure 1.3-B**) and 2-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**Figure 1.3-C**) were investigated by Penelle *et al.* to give materials that were functionalized but also could be manipulated later to give a variety of materials due to the reactivity of the siloxy group.[8] Copolymers with **1.3-B** or **1.3-C** and styrene or methyl methacrylate (MMA) showed that the feed and composition of the two monomers was nearly identical throughout the polymerization. When reactivity ratios are such that the feed and incorporation are the same, polymers with the desired amounts of each monomer can be easily synthesized. More recently, Nakahama investigated the use of 2-[(*N,N*-dialkylamino)dimethylsilyl]-1,3-butadienes.[9] The amino groups included were diethylamine (**Figure 1.3-D**), dibutylamine (**Figure 1.3-E**), pyrrolidine (**Figure 1.3-F**), and *N,N*-dimethylaminoethyl-*N*-methylamine (**Figure 1.3-G**). The anionic polymerization of these monomers was compared to that of 2-alkoxysilyl-1,3-butadienes. Molecular weights near the target molecular weight (5.0×10^3 to 2.0×10^4 g/mol) were achieved with low polydispersities (< 1.2). The authors found that these dialkylamino silyl monomers had similar reactivity to the alkoxysilyl monomers they had investigated previously. It is interesting to note that the polymerization of these monomers was relatively slow compared to most monomers under anionic conditions. Although quantitative conversions were often reached, the polymerizations took 24 to 120 h to complete when tetrahydrofuran (THF) was used as the solvent. Typically, anionic polymerizations in THF are complete in minutes to a few hours depending on the monomer.

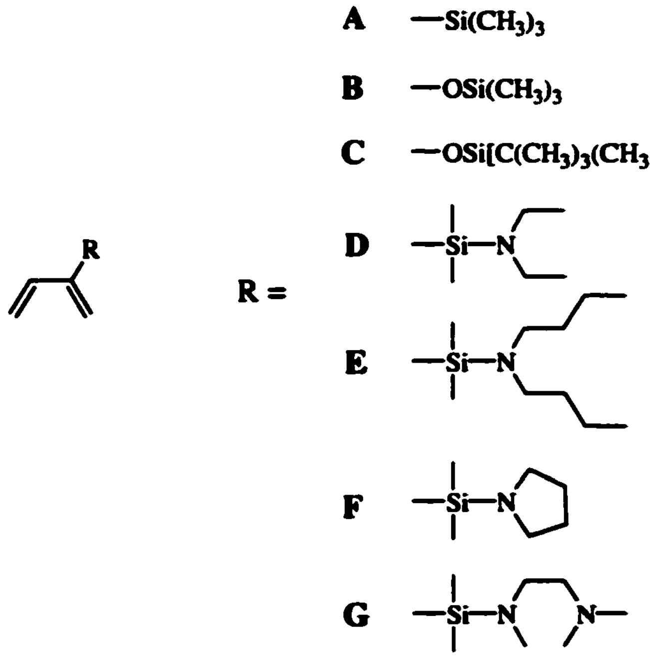


Figure 1.3. Silyl-substituted 1,3-butadienes.

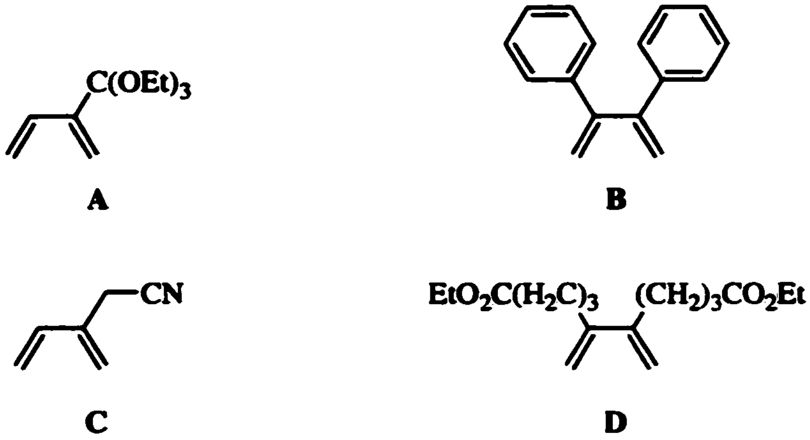


Figure 1.4. Functionalized 1,3-butadiene monomers.

Soon after silyl-functionalized monomers were investigated, Takenaka *et al.* polymerized 2-triethoxymethyl-1,3-butadiene (**Figure 1.4-A**).[10] The monomer was polymerized using free radical techniques to give molecular weights in the range of 1.0 x 10^4 to 2.0 x 10^4 g/mol with broad polydispersities and low conversions. After the polymer was synthesized, it was hydrolyzed to the corresponding carboxylic ethyl ester, which yielded a sticky polymer. It was also found that the polymerization proceeded to give almost exclusively the *cis*-1,4 microstructure. An interesting monomer that combined the structures of styrene and butadiene, 2,3-diphenyl-1,3-butadiene (**Figure 1.4-B**), was polymerized using anionic polymerization to give a polymer with quantitative conversion and low polydispersity after 168 h in THF.[11] The material had a glass transition temperature near that of styrene at 98 °C, as well as a melting temperature of 170 °C. Upon analysis of the resulting polymer, the microstructure was determined to be nearly 90% *cis*-1,4 units and the remaining was *trans*-1,4. When free radical polymerization was used instead of anionic polymerization, the T_g was higher at 116 °C but no melting point was observed. This indicates the high degree of *cis*-1,4 units in the polymer synthesized using anionic techniques leads to a material that has better order and therefore demonstrates a melting point.

To change the solvent resistance and other properties of 1,3-butadiene, Jing and Sheares investigated 2-cyanomethyl-1,3-butadiene (**Figure 1.4-C**) under free radical conditions.[12] The resulting homopolymer had a glass transition temperature of -18 °C and molecular weights from 2.0×10^4 to 6.2×10^4 g/mol. Copolymers of this monomer were also synthesized to check the possibility of utilizing **1.4-C** with styrene or acrylonitrile in industrial materials to create functionalized SBR and nitrile rubber with improved flexibility.[13] Under free radical conditions, the reactivity of **1.4-C** was much higher than styrene, so the incorporation of **1.4-C** was always higher than the feed (the same effect was even more pronounced when copolymerized with acrylonitrile). These materials (**1.4-C** with SBR and nitrile rubber) were found to have better solvent and oil resistance than the industrial materials. The Sheares group also investigated an ester-containing butadiene monomer.[14] It was found that 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (**Figure 1.4-D**) was very versatile under free radical conditions. High molecular weights of 1.25×10^5 g/mol with 60% conversion were achieved. The resulting polymer had a glass transition temperature of -37 °C and high thermal and thermooxidative stability. The polymer was hydrolyzed to give the carboxylic acid analog with a glass transition temperature of 67 °C and a carboxylate material that was only soluble in THF or in water. Studies of the copolymerization of **1.4-D** and styrene showed that styrene is more reactive under free radical conditions than **1.4-D**.

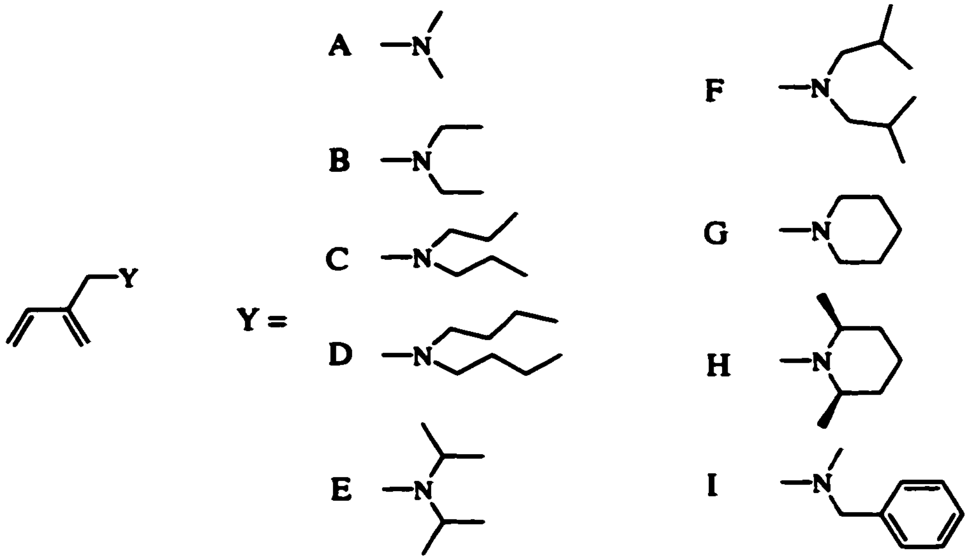


Figure 1.5. Structures of 2-(*N,N*-dialkylaminomethyl)-1,3-butadienes.

Stadler *et al.* investigated a number of 2-*N,N*-dialkylamino-substituted 1,3-butadienes.[15-21] Incorporation of amines into a polymer has several advantages. Amines often have adhesive properties and can be quaternized to yield polycations.[21] Water soluble polymers, such as these, have uses in water treatment, sealants, coatings, etc.[1] The first amine-containing diene monomer used in anionic polymerization was 2-(*N,N*-diisopropylaminomethyl)-1,3-butadiene (**Figure 1.5-E**). It was found that the monomer could only be polymerized in nonpolar solvents with only low molecular weight materials possible. A number of different amino groups ranging from diethylamine to cyclic amines, such as piperidine (**Figure 1.5-B to H**), were later investigated. Although the materials gave interesting microstructures (> 97% 1,4-addition), only low conversions and low molecular weights were achieved after 48 h of polymerization.[16] Upon investigation of the microstructures, it was found that bulkier amine groups give more *cis*-1,4 microstructure than less bulky groups.

The first quantitative conversion of a 2-(*N,N*-dialkylaminomethyl)-1,3-butadiene by anionic polymerization was achieved by Beringer and Abetz.[22] The anionic polymerization of 2-(*N,N*-dimethylaminomethyl)-1,3-butadiene (**Figure 1.5-A**) was achieved in non-polar solvents and short (< 30 minutes) reaction times. It was found that these polymers had > 95% *trans*-1,4 microstructure leading to a polymer that was semi-crystalline. The authors later used the anionic polymerization of **1.5-A** and sequential monomer addition to synthesize block copolymers with styrene and *tert*-butyl methacrylate (that would be later converted to methacrylic acid).[23] These materials were found to have interesting solubility behavior in water. They had different buffer zones which were dependant on the ratio of the acidic and basic portions incorporated into the material. These materials formed aggregates in water but were soluble in a water/THF mixture.

Due to the ease of free radical polymerization and the potential utility of butadiene-based amine monomers, the Sheares group investigated acyclic 2-(*N,N*-dialkylaminomethyl)-1,3-butadienes under traditional free radical conditions.[24] It was found that the resulting polymers from **1.5-A, 1.5-B,** and **1.5-C** had significant amounts of *cis*-1,4 incorporation into the growing chains and the glass transition temperatures of the materials were low (-30 to -60 °C). An unsymmetrical monomer, 2-[(*N*-benzyl-*N*-methylamino)methyl]-1,3-butadiene (**Figure 1.5-I**), was also polymerized under free radical conditions.[25] The polymers of **1.5-I** had modest molecular weights with typical free radical conversions and polydispersities. The polymer showed a glass transition temperature of -14 °C and 70% *cis*-1,4 microstructure.

Prior to the research described herein, only a couple of cyclic amines had been examined[16] and the significance of cyclic versus acyclic amines had not been investigated. Chapter 2 of this dissertation discusses the behavior of 2-(*N*-piperidylmethyl)-1,3-butadiene

(**Figure 1.5-G**) under free radical conditions both in bulk and emulsion polymerizations. The microstructure and thermal properties of the homopolymers and random copolymers with styrene are also addressed. Chapter 3 looks at the anionic polymerization of **1.5-G** and block copolymerization with styrene. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) showed microphase separation of these block copolymers. Quaternization of the homopolymer and phase separation of the quaternized block copolymers were also investigated.

Post-polymerization functionalization approach. The second approach to functionalize polymers is to add the functionality after the polymer has already been synthesized. This approach is especially advantageous when the desired functionality would poison the initiator or catalyst. Post-polymerization functionalization also circumvents the need to optimize the polymerization conditions for each desired monomer by allowing a variety of materials to be made from one polymer.

It is often difficult to functionalize high temperature thermoplastics because of the technique used for polymerization. These materials usually contain significant amounts of phenyl units in the backbone and are typically stronger if the backbone is made of only benzene units. Poly(*para*-phenylene)s (PPPs) are made utilizing aryl-aryl catalytic coupling chemistry. The catalyst systems used for these coupling reactions are very delicate and many of the desired functionalities (such as amines, acids, etc.) poison the catalyst. To avoid catalyst problems and to alleviate the need to optimize many systems, Bloom and Sheares took advantage of the post-polymerization approach. Poly(4'-fluoro-2,5-diphenylsulfone) was made using Ni(0)-catalyzed coupling.[26] The resulting polymer has a pendant aryl fluoride that can be used post-polymerization for nucleophilic aromatic substitution with a

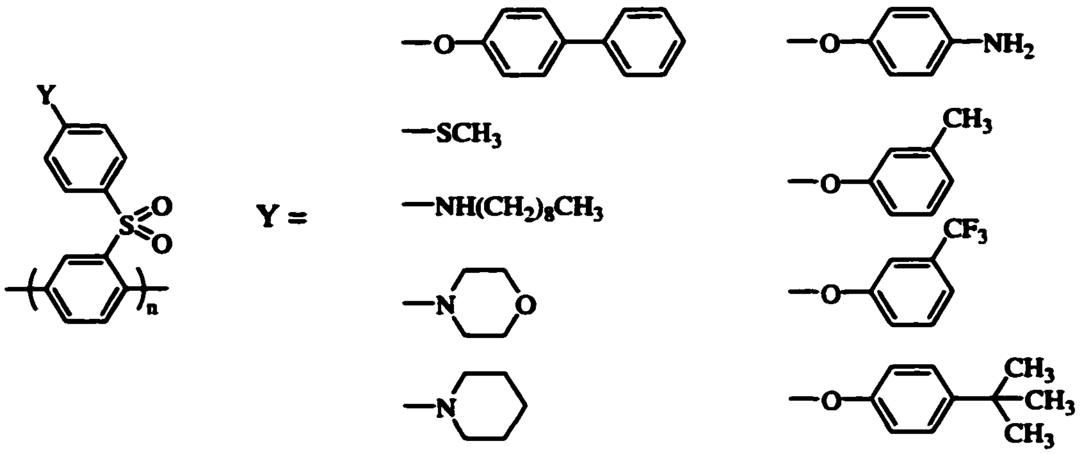
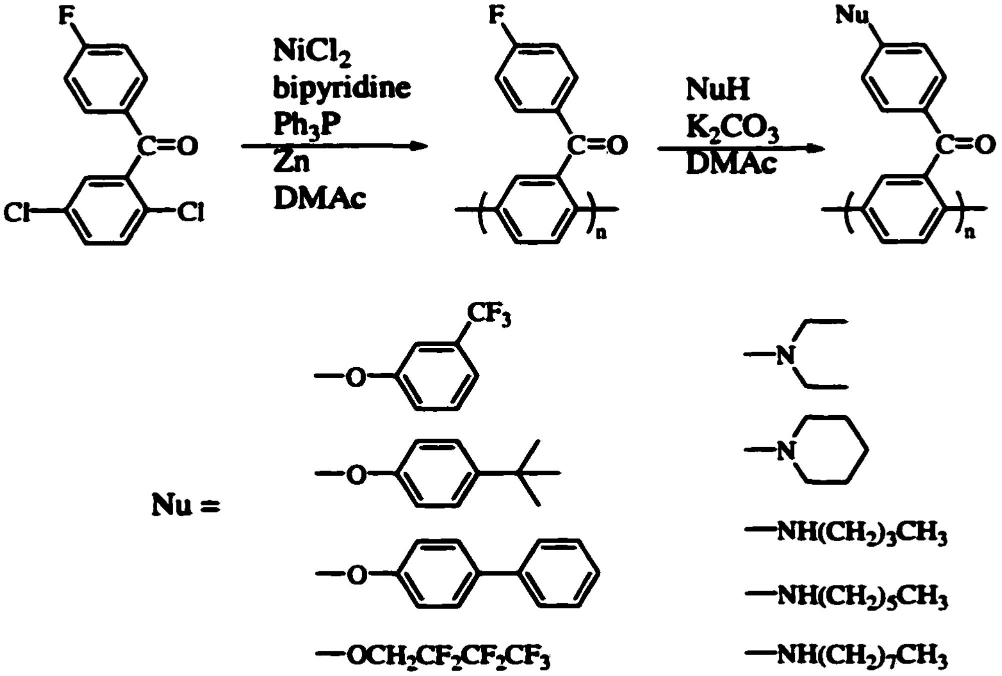


Figure 1.6. Structures of substituted poly(2,5-diphenylsulfone).



Scheme 1.1. Synthesis and substitution of substituted poly(4'-fluoro-2,5-benzophenone).

variety of nucleophiles to give a series of materials (**Figure 1.6**). The same chemistry was later used to functionalize poly(benzophenones) by polymerizing a monomer containing an aryl fluoride for post-polymerization functionalization.[27] In **Scheme 1.1**, the catalyst system and nucleophilic substitution chemistry are shown. This approach leads to materials with different thermal properties simply by changing the nucleophile chosen. This also allows for the tailoring of the parent material for a specific use by one post-polymerization reaction.

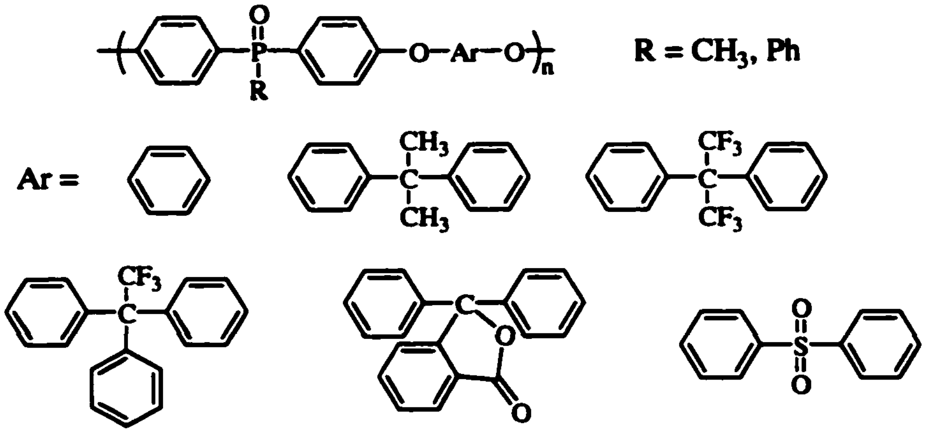


Figure 1.7. Structures of poly(arylene ether phosphine oxide) copolymers.

It is known that phosphorus compounds have fire resistant properties and are often used as additives to reduce flammability in materials.[28] The overall material might perform better under these conditions if the phosphorus was covalently bound to the material instead of being used as an additive. Additives have the problem of leaching out over time leading to material weakening and eventual material failure. If covalently bound, the additive problem could be eliminated. Researchers have looked at adding phosphorus to a material by incorporating it into the backbone (**Figure 1.7**).[29,30] This effort led to a series of copolymers made by step growth polymerization via nucleophilic aromatic substitution that contain the phosphorus in the backbone. One of the problems with the materials in **Figure 1.7** was the incorporation of the ether linkage into the polymer structure. The oxygen-carbon ether bonds were the weakest in the backbone and were the first to break under high temperatures and make the material less heat and flame-resistant. For comparison, all of the materials in **Figure 1.7** had char yields less than 25% (most were less than 16% or even 0%) at 700 °C in air, whereas the materials in **Figure 1.8** had char yields of 35% in air at 750 °C. Glass transition temperatures between the two types of materials were also very different. Those in **Figure 1.7** had glass transitions near 225 °C while those in **Figure 1.8** had glass transitions of 360 °C.

Figure 1.8. Poly(arylene phosphine oxide) materials by McGrath.

The first example of a poly(arylene phosphine oxide) that did not contain an ether linkage in the backbone was reported by McGrath *et al.*[31] McGrath used Ni(0)-catalyzed coupling to avoid the use of nucleophilic aromatic substitution and this eliminated the ether linkage from the backbone. The resulting material showed excellent thermal stability and flame resistance but there was no way to vary the structure other than the simple methyl or phenyl side chains (**Figure 1.8**). Chapter 4 of this dissertation focuses on the advantages of both phosphorus-containing materials and functionalization after the polymer has been synthesized. This approach allows for a series of materials to be made from the highly stable, flame-resistant architecture seen earlier by McGrath.

Dissertation Organization

This dissertation is organized into five chapters. The general introduction on the development of functionalized materials is the first chapter. Both the functionalized monomer approach and the functionalization of a preformed polymer are discussed. The polymerization of substituted dienes and altered high performance materials are addressed. Chapters two through four are papers that have been submitted to peer-reviewed scientific journals. The first two papers, chapters two and three, discuss the synthesis, characterization and application of amine functionalized diene polymers. The fourth chapter addresses the synthesis and characterization of high performance materials containing phosphorus and the functionalization thereafter. The final chapter, chapter five, discusses general conclusions and gives some foresight into possibilities for future research. The supplemental data for chapters two through four are contained in the appendices.

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CHAPTER 2. POLAR FUNCTIONALIZED DIENE-BASED MATERIALS. 7. BULK FREE RADICAL AND EMULSION POLYMERIZATION OF 2-(*N*-PIPERIDYLMETHYL)-1,3-BUTADIENE AND COPOLYMERIZATION WITH STYRENE

A paper submitted to Journal of Polymer Science, Part A; Polymer Chemistry. Unpublished work, copyright 2002 Wiley.

Laura A. Rusch-Salazar and Valerie V. Sheares

Abstract

High molecular weight polymer was successfully synthesized from 2-(*N*-piperidylmethyl)-1,3-butadiene using free radical polymerization techniques. Previously, only low molecular weight polymers (5.2 x 10^3 g/mol) accompanied by low conversions (13%) were synthesized from this monomer using anionic polymerization techniques. The key to higher molecular weight material is the purity of the monomer. Sulfur dioxide chemistry that we previously used to synthesize pure 2-(*N,N*-dialkylaminomethyl)-1,3-butadienes was adapted here to make 2-(*N*-piperidylmethyl)-1,3-butadiene from isoprene in > 99% purity. The bulk free radical and emulsion polymerizations were studied. Under bulk free radical conditions, traditional kinetics were observed yielding a polymer with a $<M_n>$ (number average molecular weight) of 17.1 x 10^3 g/mol and a polydispersity (PDI) near 1.4. Significantly higher molecular weights were achieved using emulsion polymerization yielding a polymer with a $<M_n>$ of 41.0 x 10^3 g/mol and a PDI of 2.0. Copolymers with styrene were also investigated using bulk free radical polymerization techniques to

synthesize materials that could be tailored by altering the feed ratio of the two monomers. This led to a series of polymers that had glass transition temperatures ranging from 24 to 77 °C. The reactivity ratios calculated from kinetic studies were found to be 2.35 ± 0.02 for 2-(*N*-piperidylmethyl)-1,3-butadiene and 0.49 ± 0.01 for styrene. These two monomers gave nonideal, nonazeotropic copolymerizations where the final materials always contained more 2-(*N*-piperidylmethyl)-1,3-butadiene than the feed.

Introduction

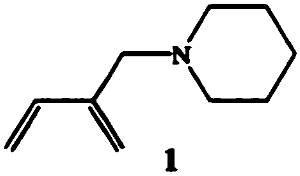
Materials containing various functional groups have become abundant in the literature due to their interesting properties and applications. Much of the research in this area has focussed on the utility of these materials as compatiblizers,[1,2] drug delivery systems[3] and easily recoverable catalysts[4] It is advantageous to covalently bond the desired functionality to the polymer instead of using an additive. This technique prevents the often volatile additives from escaping the material and eventually leading to product failure.

There are three possibilities for covalently bonding functionality to materials. The first is to functionalize a material that has already been polymerized.[2,5] This approach does not allow control of the load or distribution of the functionality. Another disadvantage is that the polymer must be reactive or have a reactive moiety in order to do chemistry on it that will lead to a functionalized material. The second approach utilizes the reactivity of the growing chain end of a linear polymer by capping this end with a desired functional group.[6] The problem with this technique is the number of end groups in linear polymers only allowing for one or two functional moieties per polymer chain. Additionally, the polymer should be made under living conditions in order to have control over the endcapping. The final option is to polymerize a monomer that contains the desired functionality. This allows for control over the load and distribution of the functional group and does not require post polymerization reactions. These considerations led us to prepare functionalized monomers.

Although functionalized styrene has been studied at length in the literature,[7-10] only a few examples of functionalized butadiene monomers can be found. This is perhaps due to the difficulty of synthesizing these monomers. As more feasible routes have emerged to synthesize functionalized dienes, producing polymers containing functionality on the diene portion of materials has become more accessible. Butadiene-based monomers ranging from 2,3-diphenyl-1,3-butadiene[11] to those containing silanes,[12-17] cyano moieties,[18,19] esters[20] and amines[21-31] have been introduced in the literature. Some of the most interesting functionalized dienes are the 2-(*N,N*-dialkylaminomethyl)-1,3-butadiene monomers. The addition of an amine onto the butadiene allows for pH dependent solubility, adhesion and crosslinking (covalent or ionic) properties that have significant academic and industrial interest.

Petzhold, *et al.* were the first to study butadienes containing the dialkylaminomethyl functionality where the amine ranged from dimethyl amine to cyclic amines such as piperidine.[22,27] These amino functionalized monomers were polymerized using anionic polymerization and the microstructures of the resulting materials were investigated using ^{1}H NMR. The polymer synthesized using 2-(*N*-piperidylmethyl)-1,3-butadiene (1) in this first study had only modest molecular weight (5.2 x 10^3 g/mol) and low conversion (13%).

This led the Sheares group to investigate similar monomers under free radical conditions.[28] Molecular weights were significantly increased over what was seen before and the thermal properties of these materials were also investigated. The monomers first studied included those containing dimethyl, diethyl and dipropyl amines. Monomer purity was significantly improved by using new synthetic routes. Molecular weights as high as 42.0 x 10^3 g/mol were achieved for the dipropyl amine monomer with a PDI of 1.8. In all cases, it was found that large amounts (75 – 80%) of the monomer repeat units had the *cis*-1,4 microstructure. The remaining units incorporated as *trans*-1,4 with small amounts of 3,4 (3 - 5%) addition. It was found that these polymers had glass transition temperatures well below ambient temperatures with values of -40 for dimethyl and diethyl and -34 °C for dipropyl.



1

Until this point, cyclic aminomethyl-1,3-butadienes have not been investigated using free radical chemistry. This monomer was investigated to see how large a role the alkyl group plays on the polymer properties. With the alkyl portion of the amine restricted compared to the acyclic alkyl amines, a difference in the microstructure of the polymer and a shift in the glass transition temperature was expected. Herein, the free radical polymerization of 2-(*N*-piperidylmethyl)-1,3-butadiene (**1**) was studied under both bulk and emulsion conditions.

Because of our interest in expanding the utility of the commercially available SBR (styrene butadiene rubber) by introduction of a polar functionality, copolymerization of **1** with styrene was also investigated under bulk free radical conditions. SBR is currently limited in its applications due to the lack of functionality. By adding the amine moiety, increased adhesion as well as altered solubility and thermal properties will result.

Experimental

Materials. All reagents were purchased from Aldrich. 2,2'-azoisobutyronitrile (AIBN) was recrystallized from methanol. Styrene was distilled from calcium hydride. Potassium persulfate was recrystallized from methanol. Distilled water was purified using a microfilter reverse osmosis system. All other chemicals were used as received.

Monomer Synthesis

2-(*N*-piperidylmethyl)-1,3-butadiene. 2-(*N*-piperidylmethyl)-1,3-butadiene was synthesized and purified as described previously.[28] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.38 (dd, *J* = 11, 18 Hz, 1H), 5.43 (d, *J* = 18 Hz, 1H), 5.15 (s, 1H), 5.13 (s, 1H), 5.07 (d, *J* = 11 Hz, 1H), 3.05 (s, 2H), 2.35 (t, *J* = 6.5 Hz, 4H), 1.56 (m, *J* = 6.5 Hz, 4H), 1.43 (m, *J* = 6.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 145.3, 138.3, 117.4, 114.3, 61.1, 55.1, 26.3, 24.7. The theoretical mass was calculated to be (for $C_{10}H_{17}N$) 151.1361 g/mol; HR-MS (high resolution mass spectrometry) showed a measured mass of 151.1364 g/mol with a deviation of 1.8 ppm.

Poly(2-[N-piperidylmethyl]-1,3-butadiene). Monomer (1.00 g, 6.61 mmol), AIBN (10.9 mg, 0.0662 mmol) and a stir bar were added to a 10 mL glass ampoule that underwent three freeze-pump-thaw cycles and was subsequently sealed under vacuum. The reaction vessel was placed in a 75 °C oil bath. After 24 h, ^{1}H NMR was taken of the polymerization mixture prior to precipitation into 10 mL of methanol (made slightly basic with 0.1 mL of 1M NaOH solution). The recovered polymer (**Table 2.1, 3**) was dissolved in a minimal amount of chloroform and reprecipitated in 10 mL of methanol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (1H), 2.79-2.89 (2H), 2.31 (4H), 1.84-2.20 (4H), 1.55 (4H), 1.42 (1H). Elemental analysis showed 78.83% C, 11.18% H, 9.09% N. The theoretical weight percentages are 79.41% C, 11.33% H, 9.26% N.

Emulsion polymerization. Water (3.6 g), SDS (sodium dodecyl sulfate, 0.050 g) and sodium bicarbonate ($NaHCO_3$) were added to a three neck 15 mL round bottom flask. The reaction vessel was fit with an overhead stirrer, a condenser and a rubber septum and degassed with argon for 20 minutes. Clean, degassed monomer (2-(*N*-piperidylmethyl)-1,3-butadiene, 2.0 g) was added via syringe. The reaction vessel was then placed in a preheated oil bath, stirred at a rate of 500 rpm and the initiator, potassium persulfate ($K_2S_2O_8$, 0.006 g) added. The reaction was allowed to proceed for a fixed amount of time ranging from 2.5 to 24 h. When a mixed emulsifier system was desired, 0.050 g of SDS and 0.030 g of the non-ionic surfactant (Triton X-100 or Triton X-405) were used. The polymerization was terminated by pouring the reaction mixture into basic methanol and adding concentrated lithium chloride solution to break up the emulsion. The polymer was reprecipitated from 10 mL of chloroform into 25 mL of methanol and dried under vacuum for 48 h before analysis.

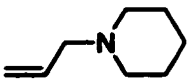
Poly(2-[N-piperidylmethyl]-1,3-butadiene-co-styrene). 2-(*N*-piperidylmethyl)-1,3-butadiene (0.50 g, 3.31 mmol), styrene (0.34 g, 3.31 mmol) and AIBN as a solution in styrene (0.33 mg, 0.0010 mmol) were added to a glass ampoule. The ampoule was subject to three freeze-pump-thaw cycles and sealed under vacuum. The reaction vessels were then placed in a preheated oil bath (75 °C) for 16 h. The polymers were precipitated in 25 mL of methanol and reprecipitated in 25 mL of methanol from 5 mL of chloroform. After drying in a vacuum oven at room temperature for 48 h, thermal analysis was completed.

Characterization. ^1H and ^{13}C NMR analyses were performed on a Varian VXR-300 and VXR-200 in deuterated chloroform at room temperature. COSY (correlation spectroscopy) and ROESY (rotational nuclear Overhauser effect spectroscopy) experiments were performed to characterize the microstructures of the polymers. Molecular weights of the polymers were measured relative to polystyrene standards with a Waters Gel Permeation Chromatograph (GPC) system consisting of a Waters 510 pump, a Waters 717 autosampler and a Wyatt Optilab DSB Interferometric Refractometer. The system was equiped with four styragel columns at 40 °C with THF as the mobile phase at a flow rate of 1.0 mL/min. Thermal data was collected from a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter at a heating rate of 20 °C/min with a helium purge and nitrogen cryofill as coolant. All glass transition temperatures are reported from the second heating of each run.

Results and Discussion

Monomer Synthesis. The syntheses of 2-(*N,N*-dialkylaminomethyl)-1,3-butadiene monomers have been investigated by our group. We found that the Frauenrath synthesis[30] was a good starting point, but higher purity was needed to optimize the polymerization of amine containing butadiene monomers. A bromination followed by a dehydrobromination of isoprene was the first method explored.[18] This technique still had the problem of lower yields, but increased the purity over the Frauenrath synthesis. Though cleaner, this route still did not give the desired purity. Very pure monomer was synthesized using an alternative route that incorporated the cheletropic addition and elimination of sulfur dioxide.[28] As one of the intermediates is a solid, the compound could be recrystallized and purified. This route only improved the yield to 20% (from the 10 to 15 % yields by the Fraunrath synthesis) but purity was > 99%. The fourth option was the Grignard nickel coupling that led to higher yields (45 – 65%) and high purity in most cases.[28] One side product of the reaction is the debromination of the amine containing portion of the coupling reaction giving **2**. In the case of 2-(*N*-piperidylmethyl)-1,3-butadiene, the monomer could not be completely purified due to this side product (**2**) so the cheletropic sulfone chemistry was used to synthesize the monomer for polymerization.

The monomer was synthesized by using a four-step approach that included the sulfonation of isoprene,[31] allylic bromination by *N*-bromosuccinimide,[32] desulfonation to give 2-bromomethyl-1,3-butadiene[32] followed by an S_N2 reaction between piperidine and 2-bromomethyl-1,3-butadiene. The advantage of this technique is the solid formed in step two (allylic bromination product) could be purified by recrystallizaiton. The product, 2-(*N*-piperidylmethyl)-1,3-butadiene, had a purity > 99%, as evidenced by GC-MS and ^{1}H NMR. The olefinic hydrogens (**Figure 2.1**) are between δ 5.0-6.5 ppm (**a-c**), the methylene peak is at δ 3.1 ppm (**d**), and the methylenes in the piperidine ring are seen from δ 1.0 to δ 2.5 ppm (**e-g**), depending on their proximity to the nitrogen.



2

Bulk Free Radical Polymerization. Polymerizations were first carried out under bulk free radical conditions to examine monomer behavior. Previously, this research group has observed a direct correlation between the amount of Diels-Alder dimer product and an increase in reaction temperature.[28] Therefore, the initiator chosen was AIBN because it has a half-life near 4 h at 75 °C. As seen by the data in **Table 2.1**, the reaction follows traditional free radical polymerization kinetics. As the molecular weight of the polymer increases with decreasing AIBN concentration, the conversion also decreases. At 1.00 mol % initiator (**3**), acceptable conversions were reached, but the molecular weight was only 7.0 x 10^3 g/mol. At these higher conversions, the polymerization solution became very viscous and stirring could no longer continue. All of the polymers were soluble in THF and chloroform as well as other organic solvents and the polydispersities were 1.2 – 1.5. Polydispersities less than 1.5 are due to loss of lower molecular weight fractions upon reprecipitation and work-up. To increase conversion further, polymerizations were run under similar conditions as those in **Table 2.1** but for 36 or 48 h. The polymers became insoluble due to the loss of control of the reaction where hot spots were created and crosslinking occurred.

In order to increase the molecular weight of the polymer, lower initiator concentrations were also studied. The molecular weight did increase, but the conversion decreased from 65% at 1.00% initiator (3) to 25% at 0.125% initiator (6). Due to the high viscosity, a molecular weight of only 17.1×10^3 g/mol could be reached. To increase molecular weight any further would require an even greater sacrifice in an already low (25%) conversion when 0.125% initiator was used.

All homopolymers synthesized under bulk free radical conditions using AIBN as the initiator yielded polymers with a microstructure containing high amounts of *cis*-1,4 units. As seen in **Figure 2.1**, the methylene hydrogens next to the olefin (d) shift from a singlet at δ 3.0 ppm to two peaks at δ 2.7 – 2.9 ppm (i). When the two methylene peaks of the polymer are integrated, the ratio of *cis* to *trans* can be calculated. The peak corresponding to the *trans*-1,4 microstructure is the peak further down field at δ 2.9 ppm and that of the *cis*-1,4 microstructure is at δ 2.7 ppm. This was verified by 2D ROESY experiments that showed the interaction of the vinyl hydrogen (h) with the methylene hydrogens (i) when the repeat unit resides in the *cis* structure. At 75 °C, 68% of the polymer was shown to be *cis*-1,4 microstructure. This is 10% lower than was seen with other 2-(*N,N*-dialkylaminomethyl)-

1,3-butadiene polymers that contained 74-80% *cis*-1,4 structure when polymerized with AIBN at 75 °C. In these comparative cases, the alkyl group is methyl, ethyl or propyl.

An alternative to bulk free radical polymerization is to carry out the reaction in a solvent. This has many advantages such as eliminating viscosity problems and hot spots, thereby gaining more control over the reaction. Generally, when polymerizations are carried out in solvent, longer times and lower initiator concentrations are required to obtain comparable conversions and molecular weights to bulk free radical polymerizations. Due to our already low conversions at low initiator concentrations, this method was not pursued. This led us to study the behavior of 2-(*N*-piperidylmethyl)-1,3-butadiene under emulsion polymerization conditions.

Contrary to bulk and solution polymerizations, emulsion polymerizations allow for an increase in the molecular weight without sacrificing the rate or conversion. In addition to the kinetic advantages, emulsion polymerization uses water as the solvent instead of organic, often toxic, solvents used for solution free radical polymerization. It also allows for immediate use as a latex without further modification, if a latex is the required form for the end use.

Emulsion Polymerization. A series of emulsion polymerizations were run to optimize the reaction conditions to achieve acceptable conversions and molecular weights above 30.0 x 10^3 g/mol. The first emulsion polymerization with 1 was done under typical conditions. The recipe includes water, water-soluble initiator, surfactant, buffer and monomer. This technique yielded a polymer with 70% conversion in 4 h. Due to the crosslinking of the material, the final product was insoluble. To optimize the conditions, emulsion polymerizations were studied using a variety of initiator systems including $K_2S_2O_8$, redox initiators, and two different organic soluble free radical initiators (AIBN and cumene hydroperoxide). Surfactant systems that were investigated include SDS, Triton X-100 and Triton X-405 and a combination of either of the nonionic surfactants with SDS (an ionic surfactant). The optimal conditions for this monomer were found to be AIBN and SDS with Triton X-405 at 80 °C. After 4 h, the polymer (**8**) had a $<M_n>$ of 41.0 x 10^3 g/mol and a PDI of 2.0. The molecular weight is significantly increased over any of the bulk free radical homopolymers and high conversion (64%) was achieved when the reaction time was increased to 16 h (**Table 2.2**, **10**). A conversion of 60 – 70% is acceptable for diene systems due to their tendency to crosslink at conversions greater than 70%.[33] Although polymer **10** was not soluble in THF (no GPC data available) the NMR was the same as polymer **8** and polymer **10** was completely soluble in chloroform. Presumably, the insolubility of **10** in THF was due to higher molecular weight than was seen for polymer **8**.

High conversions were also achieved when Triton X-100 was used instead of Triton X-405. Polymer **7** has a conversion of 57% and is completely soluble in chloroform. To achieve this conversion only required 4 h with this system, but soon after the 4 h expired, the material became crosslinked and insoluble. The microstructure of these polymers mirror that of the bulk free radical polymerizations resulting in materials that contained 60% *cis*-1,4 microstructure.

Copolymerization. Styrene was chosen as the second monomer for the copolymer materials because of its wide use in industry. The initial investigation of 2-(*N*-piperidylmethyl)-1,3-butadiene as a comonomer was done with styrene to examine how the functionalized diene behaves with styrene in polymerization. Copolymerization with styrene under bulk free radical conditions gave materials with a range of glass transition temperatures. Even with as little as 14.9% incorporation of 2-(*N*-piperidylmethyl)-1,3-butadiene into the polymer, the T_g decreased 30 °C from that of polystyrene (**Table 2.3**, **15**). Random copolymerization of styrene with the functionalized diene shows how these polymers can be tailored to a specific use.

The data for copolymerization are summarized in **Table 2.3**. Two main things to note are the increase in molecular weight with the increase of the styrene fraction and the higher incorporation of the functionalized diene monomer than the feed. The polymers were run for 16 h instead of 24 h due to high viscosity when large amounts of styrene were incorporated into the materials. Although 2-(*N*-piperidylmethyl)-1,3-butadiene was more reactive than styrene, the molecular weight of the polymer increases with increasing styrene in the feed. Styrene radical chain ends must have more difficulty terminating than 2-(*N*-piperidylmethyl)-1,3-butadiene radical chain ends, leading to an increase in molecular weight with a greater fraction of styrene in the feed. As the styrene feed increases, the number of styrene radical chain ends increase, therefore there is less termination and more propagation.

The greater amount of 2-(*N*-piperidylmethyl)-1,3-butadiene in the copolymer than the feed indicates that the butadiene monomer is more reactive than styrene under these conditions. This is clearly illustrated when the reactivity ratios are calculated. The polymerizations were monitored by ^{1}H NMR and the reactivity ratios, r_1 and r_2, were calculated from the incorporation of each monomer into the copolymer using the Mayo-Lewis equation. The r_1 value for 2-(*N*-piperidylmethyl)-1,3-butadiene was found to be 2.35 ± 0.02 and r_2 for styrene was 0.49 ± 0.01 as can be seen in **Figure 2.2**. Since the r_2 value is less than 1, styrene prefers to react with the functionalized diene. The r_1 value greater than 1 indicates that 2-(*N*-piperidylmethyl)-1,3-butadiene prefers to react with itself. These ratios suggest that the bulk free radical polymerization of styrene with **1** was a nonideal, nonazeotropic copolymerization.

Thermal Analysis. The glass transition temperature of poly(2-[*N*-piperidylmethyl]-1,3-butadiene) is 7 °C. This is much higher than we have seen for our other amine functionalized polymers that contain acyclic alkyl groups on the nitrogen. The increase in the T_g over the other poly(2-[*N,N*-dialkylaminomethyl]-1,3-butadienes) is presumably due to the restriction of the piperidyl ring allowing for less free volume. For the copolymers, the thermal data in **Figure 2.3** shows the increase in the T_g as more styrene is incorporated. **Figure 2.4** shows the T_g data according to the Fox equation. The experimental data fit very closely to the theoretical data.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

Conclusion

The free radical polymerization of a cyclic aminomethyl-1,3-butadiene monomer was described along with its thermal properties and its behavior as a comonomer. Monomer **1**, 2-(*N*-piperidylmethyl)-1,3-butadiene, followed traditional free radical kinetics. As the molecular weight of a polymer was increased, conversion was sacrificed. Although a significant improvement of the molecular weight was achieved when small amounts of initiator were used, a higher molecular weight material was still desired. This led us to study the behavior of monomer **1** using emulsion conditions. It was found that an organic initiator with a mixed surfactant system (non-ionic and ionic) worked best for **1** and led to higher molecular weight polymer than bulk free radical conditions.

Monomer **1** may be useful as a comonomer in industrial material to alter the resulting properties. To investigate the use of **1** with industrial monomers, it was copolymerized with styrene under bulk free radical conditions. These copolymers were completely random non-crystalline materials. Differential scanning calorimetry experiments showed one T_g for each of the copolymers and the glass transition temperatures fit closely to the Fox equation. Reactivity ratios were calculated using the Mayo-Lewis equation. These ratios and incorporation data showed that **1** is more reactive than styrene in this nonideal, nonazeotropic copolymerization.

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Table 2.1. Bulk free radical polymerization data for poly(2-[*N*-piperidylmethyl]-1,3-butadiene)

Sample	AIBN mol %	Conv. %	$<M_n>$ x 10^{-3}	PDI	*cis/trans*
3	1.00	65	7.0	1.3	68/32
4	0.50	52	9.2	1.5	69/31
5	0.25	40	11.4	1.5	67/33
6	0.125	25	17.1	1.2	68/32

Table 2.2. Emulsion polymerization data for poly(2-[*N*-piperidylmethyl]-1,3-butadiene) at 80 °C with AIBN as initiator

Sample	Time h	Surfactant	Conv %
7	4	TX-100/SDS	57
8	4	TX-405/SDS	17
9	8	TX-405/SDS	35
10	16	TX-405/SDS	64

Table 2.3. Copolymer data for poly(2-[*N*-piperidylmethyl]-1,3-butadiene-*co*-styrene)

Sample	Feed Diene	Incorp. Diene	$\langle M_n \rangle$ x 10^{-3}	PDI	T_g
11	100	100	11.6	1.6	7.0
12	50	65.3	20.9	1.3	23.6
13	25	36.3	32.8	1.4	51.5
14	15	21.8	55.5	1.5	66.1
15	10	14.9	85.7	1.6	76.9
16	0	0	152.3	2.0	105.6

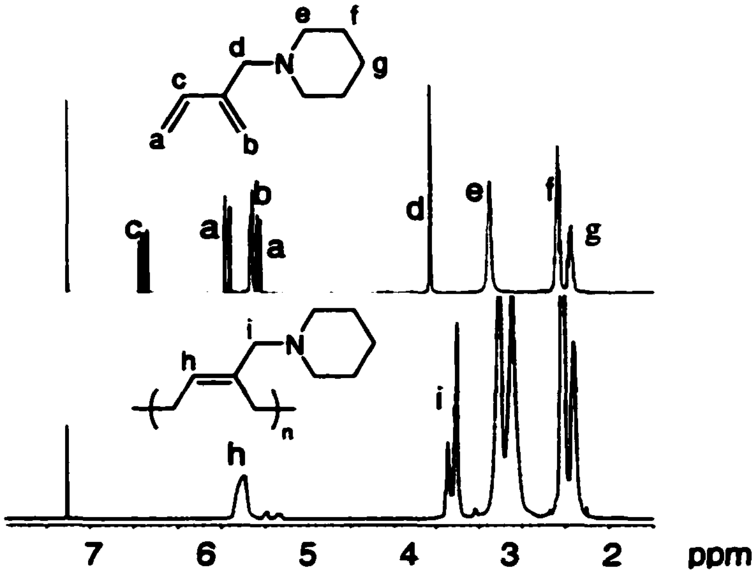

Figure 2.1. ^{1}H NMR of 2-(*N*-piperidylmethyl)-1,3-butadiene (top) and poly(2-[*N*-piperidylmethyl]-1,3-butadiene) (bottom)

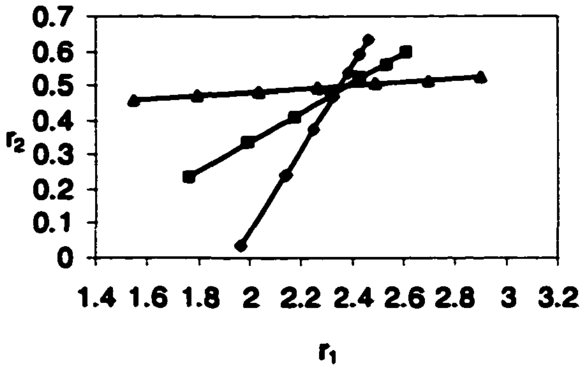

Figure 2.2. Reactivity ratios of 2-(*N*-piperidylmethyl)-1,3-butadiene and styrene

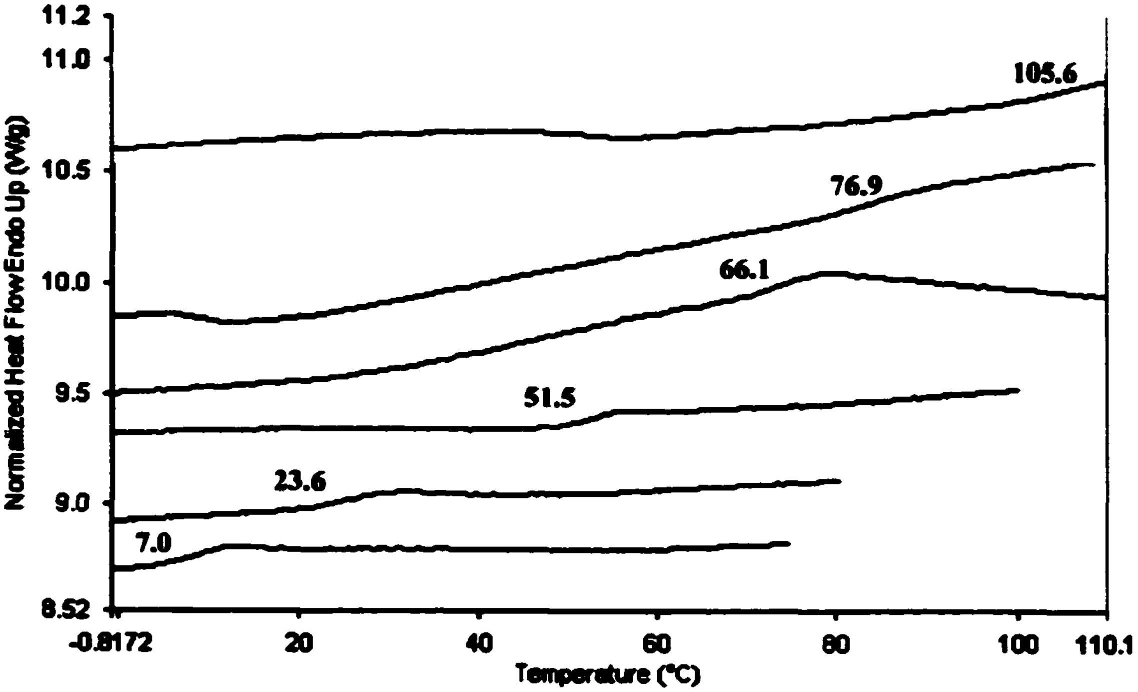

Figure 2.3. Glass transition temperatures for poly(2-[*N*-piperidylmethyl]-1,3-butadiene-co-styrene) from DSC using the second heat at 20 °C/min

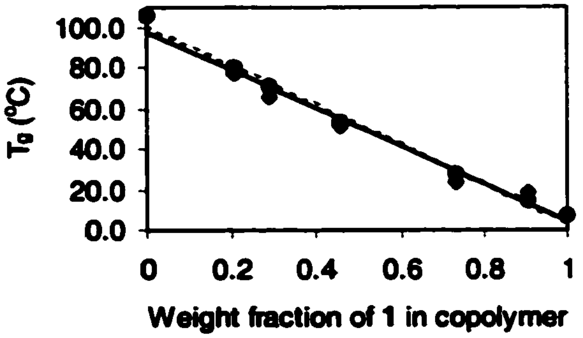

Figure 2.4. Copolymer glass transition temperatures (T_g) as a function of weight fraction of 2-(*N*-piperidylmethyl)-1,3-butadiene in the copolymer (● calculated T_g from the Fox equaiton, ◆ experimental T_g)

CHAPTER 3. POLAR FUNCTIONALIZED DIENE-BASED MATERIALS. 8. ANIONIC POLYMERIZATION OF 2-(*N*-PIPERIDYLMETHYL)-1,3-BUTADIENE AND BLOCK COPOLYMERIZATION WITH STYRENE

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Laura A. Rusch-Salazar and Valerie V. Sheares

Abstract

High molecular weight polymer was successfully synthesized from 2-(*N*-piperidylmethyl)-1,3-butadiene using anionic polymerization techniques. Previously, only low molecular weight polymers (5.2×10^3 g/mol) accompanied by low conversions (13%) were synthesized from this monomer. The key to higher molecular weight material is the purity of the monomer. Sulfur dioxide chemistry that was previously used to synthesize pure 2-(*N,N*-dialkylaminomethyl)-1,3-butadienes was adapted here to make 2-(*N*-piperidylmethyl)-1,3-butadiene (PMB) from isoprene in > 99% purity. The living anionic polymerizations were studied. Molecular weights between 5×10^3 and 2.8×10^4 g/mol were targeted and achieved with polydispersities less than 1.2. Polymers were made in cyclohexane at 10 °C in 5 minutes with quantitative conversions. Homopolymers of PMB above 3.1×10^4 g/mol synthesized by anionic methods are not soluble in THF (but are soluble in $CHCl_3$). Copolymers with styrene were also investigated using sequential monomer addition and living anionic polymerization techniques to synthesize materials that could be tailored by altering the feed ratio of the two monomers. The resulting block copolymers were made with 100% conversion and had varied phase separation depending on

composition. Quaternized PMB was made from the homopolymer and copolymers to give materials with excellent film forming properties and phase separation (also investigated by TEM). The quaternized materials with less than 75 vol% styrene were soluble in water and those with greater than 75% styrene formed cloudy solutions. Poly(PMB) was hydrogenated to achieve oxidative stability and biocompatability.

Introduction

Materials containing functionality for specialty uses such as lithography[1-3], waste water treatment[4-5] and catalyst recovery[6] are gaining consideration due to their industrial importance. Of the number of ways to incorporate functionality into a polymer, one of the most advantageous options is to attach the desired moiety to the monomer before polymerization. Many times the monomers are related to one of the two most widely used industrial monomers, styrene or 1,3-butadiene. Substituted styrene monomers have received significant attention due to the ease of monomer synthesis and polymerization.[7-10]

It is only recently that 1,3-butadienes analogs have recieved increasing attention. This is presumably due to the difficulty in synthesizing these compounds. Recently, moieties such as silanes, ethers, esters, nitriles and amines have been investigated.[11-31] Of these, one of the most interesting is the amine group due to the amine's versatility and potential for useful and interesting properties. The possibilities include, but are not limited to, crosslinked (ionically or covalently), chelated (to metals) and quaternized materials that can be used as thermosets, metal ligands and water soluble polymers.

Petzhold *et al.* were the first to study butadiene-based monomers containing the dialkylaminomethyl functionality where the amine ranged from diethyl amine to cyclic amines such as piperidine. These amino functionalized monomers were polymerized using anionic polymerization and the microstructures of the resulting materials were investigated using ^{1}H NMR. The polymer synthesized using 2-(*N*-piperidylmethyl)-1,3-butadiene in this first study had only modest molecular weight (5.2 x 10^3 g/mol) and low conversion (13%) after a reaction time of 48 hours.[22,27]

Similar monomers were investigated using free radical polymerization by the Sheares group.[28] Increased molecular weights were achieved over previous reports of poly[2-(*N,N*-dialkylaminomethyl)-1,3-butadienes]. The Sheares group also investigated the thermal properties and microstructure of these materials. The monomers first studied included those containing acyclic amines. Monomer purity was significantly improved by using new synthetic routes and molecular weights as high as 42.0 x 10^3 g/mol were achieved for the dipropyl amine monomer with a PDI of 1.8. When these monomers were polymerized anionically by Percec and Stadler, high percentages of *trans*-1,4 addition of the monomers were seen. In the case of the free radical polymerizations, it was found that *cis*-1,4 microstructure was incorporated in large amounts (75 – 80%). The remaining units incorporated as *trans*-1,4 with small amounts of 3,4 (3 - 5%) addition. These materials had glass transition temperatures well below ambient temperatures with values of -40 for dimethylamine and diethylamine monomers and -34 °C for the dipropylamine monomer.

More recently, Beringer and Abetz studied the 2-(*N,N*-dimethylaminomethyl)-1,3-butadiene.[27] Quantitative conversion was achieved for this monomer using anionic polymerization. Block copolymers containing 2-(*N,N*-dimethylaminomethyl)-1,3-butadiene, styrene and *t*-butylmethacrylate (to be converted to methacrylic acid) were also synthesized. These materials were found to have very complex solubility behavior. Portions of the material are soluble in organic solvents while others are soluble in water. This led them to use a water/THF mixed solvent system to carry out studies on these materials. Beringer and Abetz found the hydrodynamic volume of these materials increases with decreasing pH. Freeze fracture TEM showed the aggregates made vesicles at lower pH values (pH = 4) but as the system became more basic (pH = 10) less uniform spherical structures were seen.

Anionic polymerization is a useful method for synthesizing polymers due to the advantages of controlled molecular weight, short reaction times, low polydispersities and sequential monomer addition. Anionic polymerization can therefore lead to materials that have a specific structure and length. Block copolymers are useful in a number of applications such as compatiblizers, thermoplastic elastomers, gas separation membranes and surfactants to name a few.[32,33] These block copolymers self assemble to give a number of different structures with very small domains compared to those achieved by physical etching. If the monomers are chosen carefully for these materials, the microdomains could be plated with a conductive material that adheres to one of the portions contained in the block copolymer using electroless plating.[1-3] Electroless plating has been used previously to plate films with palladium and subsequently copper.[34,35]

In addition to the advantage of an amine being a good chelating agent, it also can be quaternized to yield a water soluble polymer. Quaternization of an amine containing polymer gives materials that are ionomers and polyelectrolytes. Depending on the degree of quaternization (the portion of ionic groups in the polymer) the materials can be used as flocculants, coagulants, sealants, etc.

Herein, we utilize the advantages of anionic polymerization and the amine moiety to create a polymer possessing defined molecular weight containing functionality.

Homopolymers of 2-(*N*-piperidylmethyl)-1,3-butadiene (PMB) and copolymers containing PMB and styrene were synthesized with quantitative conversions. These materials were also hydrogenated for increased stability and quaternized for water solubility.

Experimental

Materials. All reagents were purchased from Aldrich and used as received unless otherwise noted. Styrene was purified using a basic alumina column and distillation over dibutyl magnesium under vacuum. Cyclohexane was purchased from Fisher Scientific and was washed with concentrated sulfuric acid, water and 1.0 M sodium hydroxide. The cyclohexane was then dried over sodium and distilled under argon. Initiator, *sec*-butyl lithium, was purchased from FMC Lithium Div. and used as received. Tetrahydrofuran (THF) was dried over sodium and distilled under argon.

Characterization. ^1H and ^{13}C NMR analyses were performed on a Varian VXR-300 in deuterated chloroform at room temperature. Molecular weights of the polymers were measured relative to polystyrene standards with a Waters Gel Permeation Chromatograph (GPC) system consisting of a Waters 510 pump, a Waters 717 autosampler and a Wyatt Optilab DSB Interferometric Refractometer. The system was equipped with four styragel columns at 40 °C with THF as the mobile phase at a flow rate of 1.0 mL/min. In addition, molecular weights were determined using an 18 angle online multiangle lase light scattering detector (Wyatt DAWN EOS) connected to the GPC system. Glass transition temperatures were collected from a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter at a heating rate of 20 °C/min with a helium purge and nitrogen cryofill as coolant. All glass transition temperatures are reported from the second heating of each run. Degradation temperatures were measured on a Perkin-Elmer TGA 7 with a heating rate of 10 °C/min. Thin films were collected onto 200 mesh nickel grids and stained with osmium tetroxide vapor (2% osmium tetroxide in D_2O) for two hours. Images were collected using a JEOL 1200EX scanning and transmission electron microscope (TEM) (Japan Electron Optics Laboratories) at 80 kV with a Megaview III digital camera system (Soft Imaging Systems).

2-(*N*-piperidylmethyl)-1,3-butadiene. 2-(*N*-piperidylmethyl)-1,3-butadiene (PMB) was synthesized and purified as described previously.[28,29] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.38 (dd, J = 11, 18 Hz, 1H), 5.43 (d, J = 18 Hz, 1H), 5.15 (s, 1H), 5.13 (s, 1H), 5.07 (d, J = 11 Hz, 1H), 3.05 (s, 2H), 2.35 (t, J = 6.5 Hz, 4H), 1.56 (m, J = 6.5 Hz, 4H), 1.43 (m, J = 6.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 145.3, 138.3, 117.4, 114.3, 61.1, 55.1, 26.3, 24.7. The theoretical mass was calculated to be (for $C_{10}H_{17}N$) 151.1361 g/mol; HR-MS (high resolution mass spectrometry) showed a measured mass of 151.1364 g/mol with a deviation of 1.8 ppm.

Poly(2-(*N*-piperidylmethyl)-1,3-butadiene). PMB was purified by allowing it to stir over dibutyl magnesium for twenty minutes before vacuum distillation. To a 25 mL flame-dried round-bottom flask equipped with a magnetic stir bar and a septum was added PMB (0.5 mL, 2.98 mmol), cyclohexane (4.5 mL) and *sec*-butyl lithium (10 μL of 2.5 M solution in heptane). The reaction vessel was kept at 10 °C for 5 minutes. The polymer was terminated using 0.1 mL of degassed methanol and precipitated into 10 mL of methanol. The final white material was dried under vacuum for 48 h before analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (1H), 2.79-2.89 (2H), 2.31 (4H), 1.84-2.20 (4H), 1.55 (4H), 1.42 (2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ `36.39, 136.36, 128.35, 66.50, 58.59, 58.09, 54.91, 36.53, 29.82, 29.65, 27.07, 26.44, 24.91. Elemental analysis showed 78.83% C, 11.18% H, 9.09% N. The theoretical weight percentages were 79.41% C, 11.33% H, 9.26% N.

Hydrogenation. Hydrogenation of the homopolymer was carried out in a Parr high pressure reactor. Poly(PMB) (0.25 g) was dissolved in 1 M HCl (5.0 mL) and placed into the reactor. Palladium on carbon was then added (0.2 g of 5% Pd on carbon) and the reactor was sealed. Hydrogen gas was pumped into the reactor using an air pump to 1100 psi. The reaction was heated to 150 °C for 24 h. The solution was filtered and the eluent made basic with 1 M NaOH solution causing the hydrogenated polymer to precipitate from the solution. The polymer was reprecipitated from 2 mL chloroform into 10 mL methanol. The hydrogenation proceeded in better than 98% conversion. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (4H), 2.10 (2H), 1.56 (4H), 1.42 (2H), 1.26 (6H), 0.85 (1H).

Quaternization. The quaternization was carried out as described previously.[36] The quaternization proceeded in better than 98% conversion. ^{1}H NMR (300 MHz, D_2O): δ 5.87-6.04 (1H), 3.89-3.99 (2H), 2.97-3.03 (3H), 2.33-2.30 (4H), 1.88 (8H), 1.56 (2H).

Copolymer Synthesis. Block copolymers were synthesized following similar conditions to those listed for synthesis of the homopolymer. Instead of terminating with methanol, a calculated amount of styrene in THF (1:2 by volume) was added via syringe to extend the poly(PMB) with styrene. The reaction was carried out at 10 °C and was terminated with 0.1 mL of degassed methanol after 1 h. The resulting polymer was precipitated into 20 mL of methanol and dried under vacuum for 48 h before analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04-7.08 (3H), 6.49-6.57 (2H), 5.34 (1H), 2.79-2.89 (2H), 2.31 (4H), 1.84-2.20 (4H), 1.42-1.55 (9H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 136.41, 136.19, 128.69, 128.50, 128.26, 127.84, 125.89, 125.72, 66.54, 58.23, 55.26, 54.91, 40.49, 36.52, 29.82, 27.17, 27.06, 26.81, 26.45, 24.91.

Results and Discussion

Synthesis of Poly(PMB). Monomer, 2-(*N*-piperidylmethyl)-1,3-butadiene (PMB), was synthesized using sulfur dioxide chemistry previously used to make these types of monomers in high purity. Although the monomer yield was relatively low (20%), the purity was >99% which is necessary for successful anionic polymerization. Previously, Stadler *et al.* polymerized PMB under anionic conditions in benzene at room temperature and only 13% conversion was reached after 48 h yielding a polymer with a number average molecular weight of 5.2 x 10^3 g/mol.[22] When using the sulfur dioxide chemistry to make PMB, the resulting polymerization in benzene at room temperature was complete in less than 20 seconds with *sec*-butyl lithium as the initiator. The resulting polymer had a broad molecular weight distribution. Therefore, cyclohexane was used instead of benzene to gain control over the polymerization rate. The polymerizations were carried out at cooler temperatures (10 °C) and in fairly dilute solutions (10% monomer). The polymerizations were complete in 5 minutes with 100% conversion (**Scheme 3.1**).

One of the advantages of anionic polymerization is the ability to target specific molecular weights. Here, molecular weights of 5.0 x 10^3 to 28.0 x 10^3 g/mol were targeted. By controlling the ratio of monomer to initiator concentrations, these molecular weights were achieved (**Table 3.1**). Number average molecular weights ($<M_n>$) and polydispersities of the homopolymers were measured using gel permeation chromatography (GPC). The molecular weight data were a little higher than the targeted molecular weights, presumably due to some impurities in the monomer or solvent which led to poisoning of a small amount of the initiator. This gave a higher effective initiator concentration and ultimately higher molecular weights. As expected from anionic polymerization, the polydispersities were low (1.12-1.19) as seen in **Table 3.1**. Higher molecular weights were achieved, but any above 31.5 x 10^3 g/mol were insoluble in THF. This is presumably due to the predominant *trans*-1,4 microstructure in the polymers leading to greater solvent resistance.

Poly(PMB) Microstructure. The microstructure of these polymers was dependent on a number of factors. The effect of the solvent was the first to be investigated. Four possibilities for the microstructure exist and are shown in **Scheme 3.1**. In all cases, only *cis*-1,4, *trans*-1,4 and 3,4 incorporations was seen and no 1,2 addition was ever observed. **Figure 3.1a** shows the ^{1}H NMR of poly(PMB). When cyclohexane was used as the solvent, the amount of *trans*-1,4 addition is lower than when an aromatic solvent was used (benzene or toluene). In toluene, the amount of *trans*-1,4 structure was 79%. Aromatic solvents facilitate more separation of the chain end anion and lithium counter ion than cyclohexane. This allowed for freer transition to the *trans* conformation before the next monomer added to the chain end.

It was found that the microstructure also depends on the target molecular weight. For those materials where the target molecular weight was 5.0 x 10^3 to 28.0 x 10^3 g/mol (1-6), the amount of *trans*-1,4 units in the product increased from 35% (1) to 71% (6). To investigate this effect, polymerizations were run using constant initiator concentration and the monomer volume was varied to achieve the target molecular weights. When the initiator concentration is held constant, the amount of *trans*-1,4 incorporation into the materials was nearly constant at 60%. The governing effect for the *cis*-*trans* incorporation must therefore depend on the concentration of the active chain ends and the ability of the chain ends to interconverted between the *cis* and *trans* configurations. If the concentration of chain ends was high (target molecular weight is low), more aggregation was present especially in a non-polar solvent like cyclohexane and addition of the next monomer was also faster. This caused more *cis*-1,4 addition because of the monomer approach for addition. Stadler showed that the monomer adds in a *cis*-oid fashion.[23] When initiator concentration was high, the next monomer adds to the chain end before the transition to the more stable *trans* form is made.

The final factor that affected the microstructure was the temperature at which the polymerization was run. At lower temperatures (0 °C) even greater amounts of *trans*-1,4 addition was seen. Poly(PMB) synthesized at 0 °C in toluene had nearly 90% *trans*-1,4 nanostructure. The larger amount of *trans*-1,4 addition at lower temperatures was due to slower addition and the chance for the chain end to convert to the lower energy *trans* conformation.

Thermal Properties of Poly(PMB). Poly(PMB) had typical weight loss for these types of diene-based materials. The 5% weight loss under nitrogen was 320 °C and that under air was 310 °C. As expected, the glass transition temperature (T_g) increased with increasing molecular weight. For polymers with a number average molecular weight of 31.2 x 10^3 g/mol, the T_g was found to be 13 °C. The materials with smaller number average molecular weights had glass transition temperatures of -21.6 and -2.1 °C for **1** and **2**, respectively (**Table 3.1**). The polymers with molecular weights above 18.0 X10^3 g/mol appeared white and were soft. Those with lower molecular weights were clear viscous materials and demonstrated adhesive properties.

Hydrogenation of Poly(PMB). Hydrogenation of diene-based polymers is important for long-term applications where degradation and crosslinking of the material would be detrimental to the material's performance. Hydrogenation of the double bond left in the backbone should also increase biocompatibility for applications such as drug delivery. Although poly(butadiene) and even poly(isoprene) are easily hydrogenated, polymers with larger substituents (such as poly(PMB)) are much more difficult to hydrogenate. The homopolymer was hydrogenated using hydrogen gas and palladium on carbon as the catalyst (**Scheme 3.2**). The reaction was carried out in a high pressure reactor to enable 1100 psi of hydrogen to be applied to the material. It was found that the reaction needed to be done in acid to prevent the nitrogen in the polymer from chelating to the palladium catalyst. Any attempts to do the reaction under neutral or slightly acidic conditions failed to hydrogenate the polymer. Once all amine sites were protonated, the hydrogenation reactions proceeded in nearly quantitative conversions as evidenced by the ^{1}H NMR (**Figure 3.1**). When comparing the NMR of poly(PMB) to the hydrogenated version, the disappearance of the vinylic hydrogen at δ 5.34 ppm was seen. The resulting materials showed a glass transition at -4 °C (30.0 x 10^3 g/mol polymer was used), a decrease of nearly 20 °C from the original homopolymer. The decrease in the T_g is presumably due to the increased flexibility of the chains as well as the atactic nature of the hydrogenated material.

Quaternization of Poly(PMB). Quaternization of the poly(PMB) was carried out to create a material that was soluble in water. The homopolymer was methylated using dimethylsulfate and proceeded with quantitative conversions (**Scheme 3.3**). The ^{1}H NMR of quaternized poly(PMB) shows the shift of both the vinylic hydrogen and the methylene hydrogens adjacent to the nitrogen as seen in **Figure 3.2**. The vinylic hydrogen shifts from δ

5.34 ppm to 5.87-6.04 ppm, the methylene shifts from δ 2.79-2.89 to 3.89-3.99 ppm and the appearance of the methyl group at δ 2.97-3.03 ppm. The resulting material was soluble in water, methanol and ethanol, where poly(PMB) is soluble in non-polar common organic solvents such as cyclohexane, chloroform and THF. Due to the number of amine groups on poly(PMB), it is also soluble in 1 M HCl. The quaternized material had an increased glass transition temperature from poly(PMB) to 43 °C. Any desired amount of quaternization could be achieved depending on the amount of dimethylsulfate added to the reaction mixture. This led to a series of materials that range from water insoluble (little to no quaternization) to ionomers (10% quaternization) to fully quaternized, water soluble species.

Copolymers. As discussed previously, advantages of anionic polymerization include the ability to obtain controlled molecular weight and low polydispersities. But, another advantage is the living nature of the polymerization that allows for chain extension and the synthesis of block copolymers. Block copolymers with varying composition and molecular weights were constructed from PMB and styrene. It was found that PMB is more reactive under anionic conditions in cyclohexane than styrene. This means that the PMB must be polymerized first in order to cross over to the second monomer, styrene as seen in **Scheme 3.4**. Due to the extremely slow polymerization rate of styrene in cyclohexane, the polarity of the solution was increased by the addition of THF. THF is usually a very good solvent for anionic polymerization because it separates the counter ion (Li^+) from the anionic chain end allowing for an increase in the polymerization rate. In the case of PMB though, even when small amounts (2%) of THF were added to the reaction mixture, little to no polymer was synthesized. This was explained previously by Stadler who found that 2-(*N,N*-dialkylaminomethyl)-1,3-butadiene monomers must coordinate to the chain end cation (Li^+)

for propagation to occur.[25] If THF is added, the THF preferentially coordinates to the Li^+ instead of the monomer, and propagation is halted. Thus, PMB was polymerized first in cyclohexane and the styrene (in THF) was added subsequently after the completion of PMB.

Materials with different volume fractions and varied molecular weights were synthesized (**Table 3.2**). In the case of polymer 7, 25 vol% PMB ($<M_n>$ of poly(PMB) portion was 17.0 x 10^3 g/mol with a PDI of 1.16), an aliquot was removed from the polymerization after the completion of the first block (poly(PMB)) to obtain molecular weight data from GPC and to verify the living character. The molecular weight of the polymer after polymerization of the styrene showed an increase to a number average molecular weight of 66.0 x 10^3 g/mol with a PDI of 1.06 (**Figure 3.3**). This material showed two glass transition temperatures of 11 and 106 °C corresponding to the poly(PMB) block and poly(styrene) block respectively.

A series of materials with different molecular weights and 25% PMB were synthesized to look at changes in domain size in phase separation and properties. All copolymers (7-12) are white and soluble in common organic solvents such as chloroform, tetrahydrofuran, etc. For the series of materials with varying amounts of PMB, those with higher amounts of PMB are softer due to the increased amounts of the lower T_g material (PMB). The solubility is similar to the copolymers discussed above. **Table 3.2** shows all copolymers synthesized and their molecular weight data. Experimental molecular weights are close to the target molecular weights in all cases. Light scattering of the copolymers (13-15) showed molecular weights higher than expected. In-line light scattering with 100% mass recovery was used to calculate the molecular weight and PDI of these materials. **Figure 3.4** shows the change in incorporation of PMB for polymers **13-15**. This is a noticeable increase in the poly(PMB) and the decrease in the poly(styrene) across the NMR spectra.

Quaternization of Block Copolymers. Block copolymers were quaternized in the same manner as poly(PMB). Due to the varying composition of the copolymers, the solubility of the materials changed with the increasing incorporation of quaternized poly(PMB). Those materials containing less than 30% PMB units were soluble in chloroform but not in water or methanol. Materials containing more PMB (60%) formed cloudy solutions in both water and chloroform. If the material contained enough PMB (80%), the quaternized copolymer was soluble in water and methanol.

Microphase separation. Films of the above polymers were made using a 1.0% solution of the polymer in toluene. The solution was dropped onto water followed by deposition onto a nickel grid for TEM investigation. A reservoir of toluene was used to saturate the atmosphere and ensure slow evaporation of the solvent. Slow evaporation allowed the polymer enough time to phase separate. After annealing the film at 120 °C for 72 h, the films were investigated by TEM. The poly(PMB) blocks were stained with OsO_4 and are the black portions in the TEM images and the poly(styrene) blocks are not stained and appear white. It was seen from **Figure 3.5a-c** that the amount of PMB included in the sample alters the phase separation pattern. When a small amount of PMB is used, the small spheres of poly(PMB) were seen surrounded by the poly(styrene) matrix (**Figure 3.5a**). At the same molecular weight, when PMB is 80% of the material (**Figure 3.5c**), a different pattern was seen and the poly(PMB) was the matrix. At 60% PMB (**Figure 3.5b**), the TEM shows more equal volume of the two phases.

Materials that had been quaternized were also investigated by TEM. Polymer 9 was quaternized and the TEM showed a significant difference in both domain size and phase separation. The quaternized material has a much more ordered pattern than the non-quaternized version (**Figure 3.6**) and larger domains. Continued investigation of the phase separation of nonquaternized, partially quaternized and fully quaternized materials will be used as well as for triblock copolymers. The phase separated materials characterized here will be investigated for their use in electroless plating of conductive metals.

Conclusion

Anionic polymerization was used to polymerize 2-(*N*-piperidylmethyl)-1,3-butadiene (PMB) in quantitative conversions. These amine containing polymers have many possibilities for applications as a specialty material in the areas of water soluble polymers, biocompatible materials and coatings. To allow the use of poly(PMB) in biological applications it must hydrogenated to eliminate the double bond in the backbone. The post-polymerization reactions of hydrogenation and quaternization were carried out in nearly quantitative conversions. Quaternized materials were water soluble and could be used in applications such as telechelics, ionomers and polyelectrolytes depending on the extent of quaternization.

Due to the living nature of anionic polymerization, block copolymers with styrene were also synthesized. As expected, styrene was less reactive than PMB and was therefore the second block to be polymerized. This control over polymerization allows for block copolymers to be synthesized, as discussed, but also amphiphilic triblock copolymers. The quaternized version of the block copolymers gave very interesting phase separation and solubility behavior. After the material was quaternized, the domains in the film were not only larger but also much more ordered. The solubility depended highly on the degree of ionization of the backbone and ranged from polymers soluble in organic solvents such as chloroform (with small amounts of PMB) to water soluble materials (large amounts of PMB).

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Table 3.1. Molecular weight, microstructure and glass transition temperature data for poly(PMB).

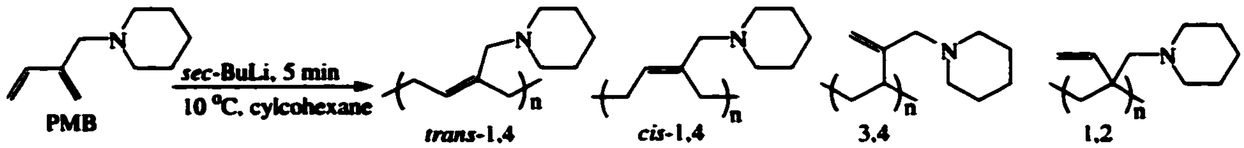
Sample	Target M_n[a] x 10^{-3}	$<M_n>$[b] x 10^{-3}	PDI[b]	% *trans*[c]	T_g[d]
1	5.0	6.3	1.12	35	-21.6
2	12.5	14.0	1.13	51	-2.1
3	18.0	22.0	1.14	58	2.4
4	20.0	25.0	1.19	67	4.3
5	25.0	28.0	1.17	68	8.0
6	28.0	31.2	1.16	71	13.9

[a] g/mol, [b] from GPC using polystyrene standards g/mol, [c] from NMR, [d] from DSC using the second heat at a heating rate of 10 °C/min

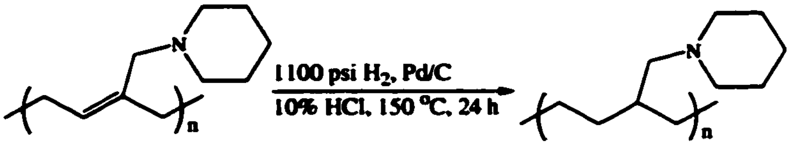
Table 3.2. Molecular weight and incorporation data for poly(PMB-*b*-styrene).

Sample	Volume % PMB	Target M_n^{a} x 10^{-3}	$\langle M_n \rangle$^{b} x 10^{-3}	PDI^b
7	25	60.0	66.0	1.06
8	25	45.5	49.4	1.56
9	25	30.5	30.1	1.65
10	25	25.5	26.6	1.32
11	25	22.7	21.7	1.38
12	25	17.2	17.7	1.30
13	30	30.6	41.1	1.05
14	60	30.4	29.6	1.07
15	80	29.6	43.2	1.06

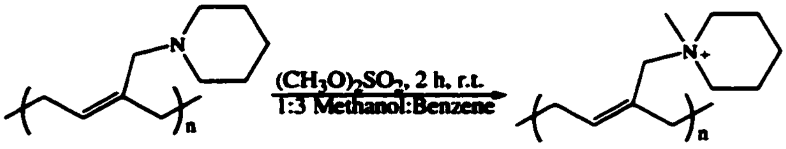
[a] g/mol, [b] from GPC using polystyrene standards g/mol, [c] from light scattering



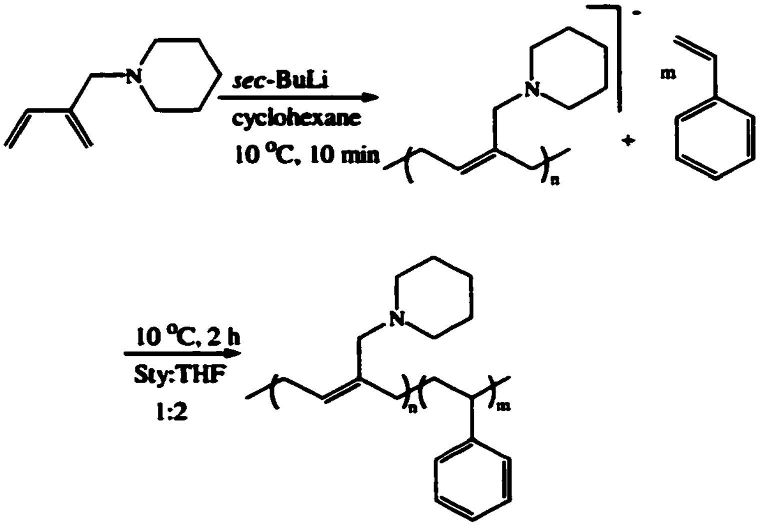
Scheme 3.1. Anionic polymerization of PMB including all possible microstructures.



Scheme 3.2. Hydrogenation of poly(PMB).



Scheme 3.3. Quaternization of poly(PMB).



Scheme 3.4. Copolymerization of PMB and styrene.

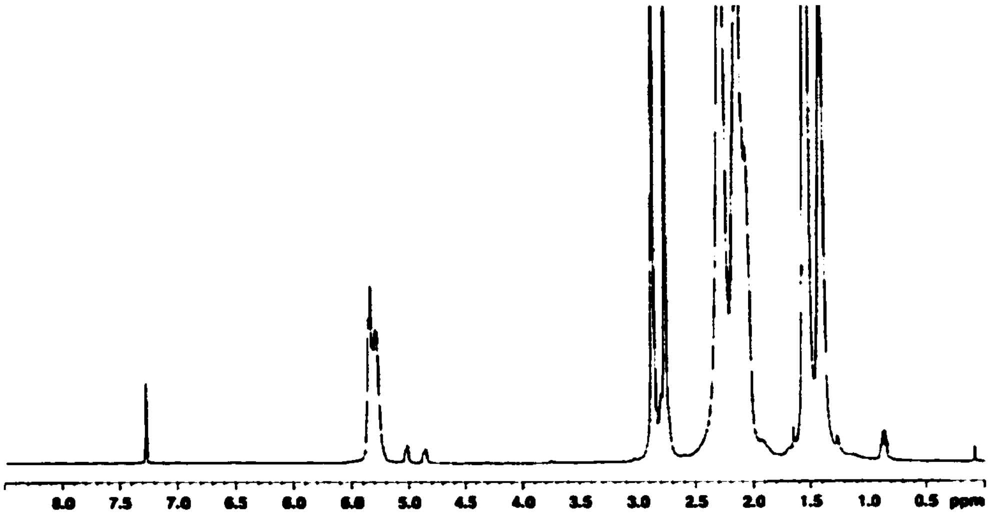


Figure 3.1a

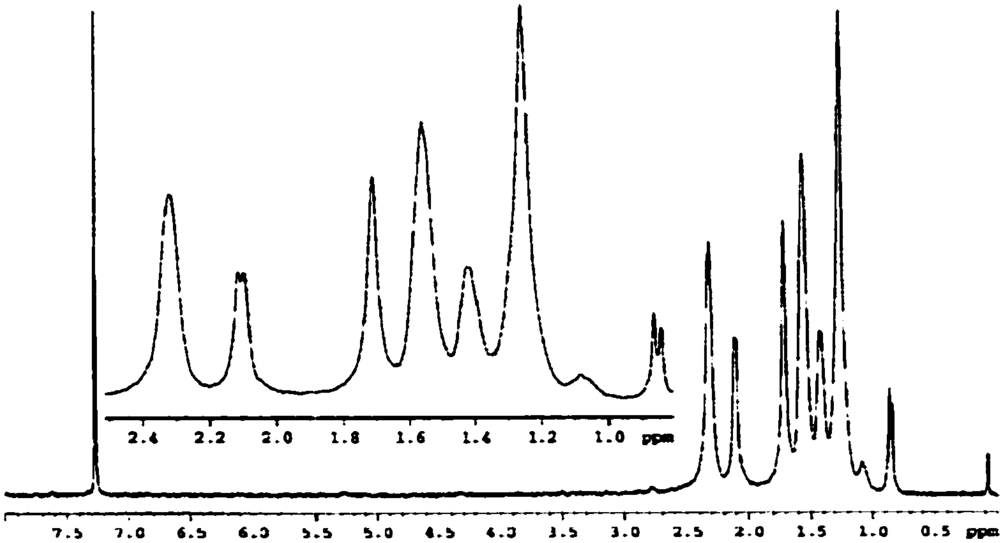


Figure 3.1b

Figure 3.1. ^{1}H NMR of (a) poly(PMB) and (b) hydrogenated poly(PMB).

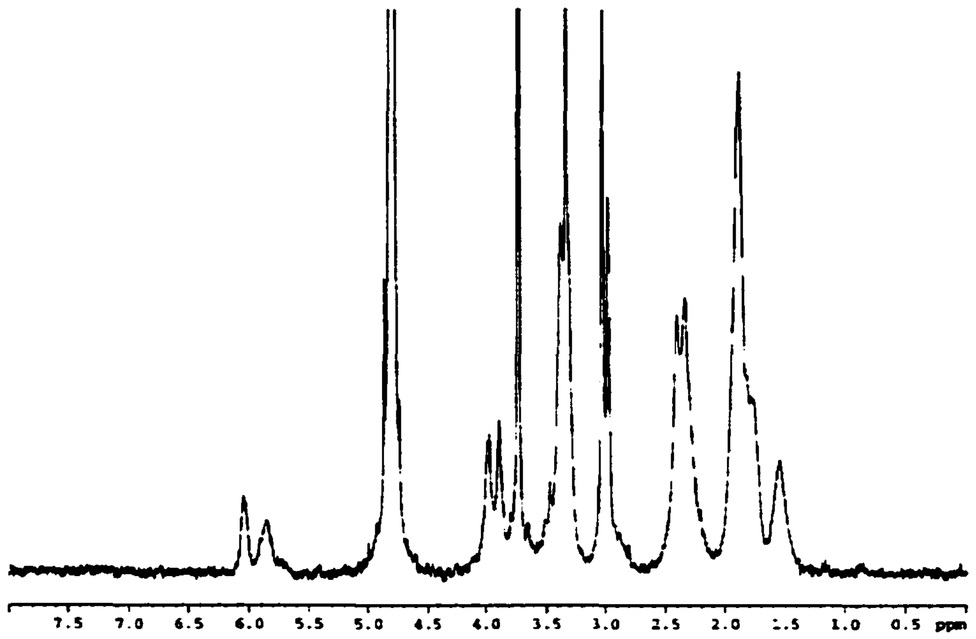


Figure 3.2. ^{1}H NMR of quaternized poly(PMB).

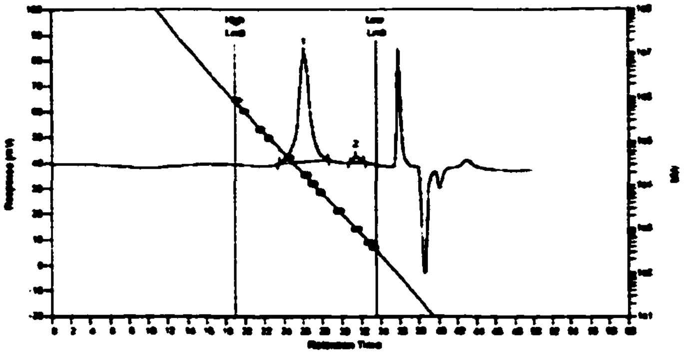


Figure 3.3a

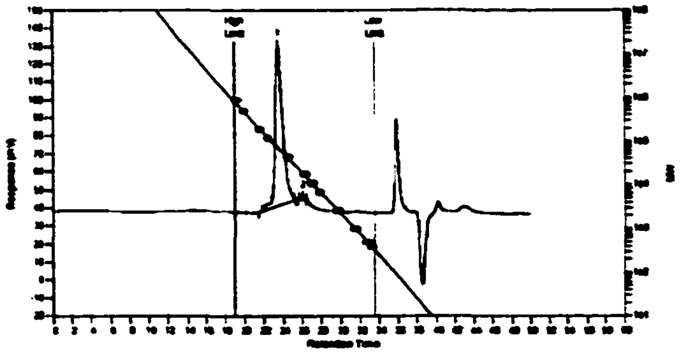


Figure 3.3b

Figure 3.3. GPC of copolymer containing 25% PMB. (a) Block A containing PMB (17.0 x 10^3 g/mol, PDI = 1.16) and (b) both blocks of the copolymer (7) (66.0 x 10^3 g/mol, PDI = 1.06).

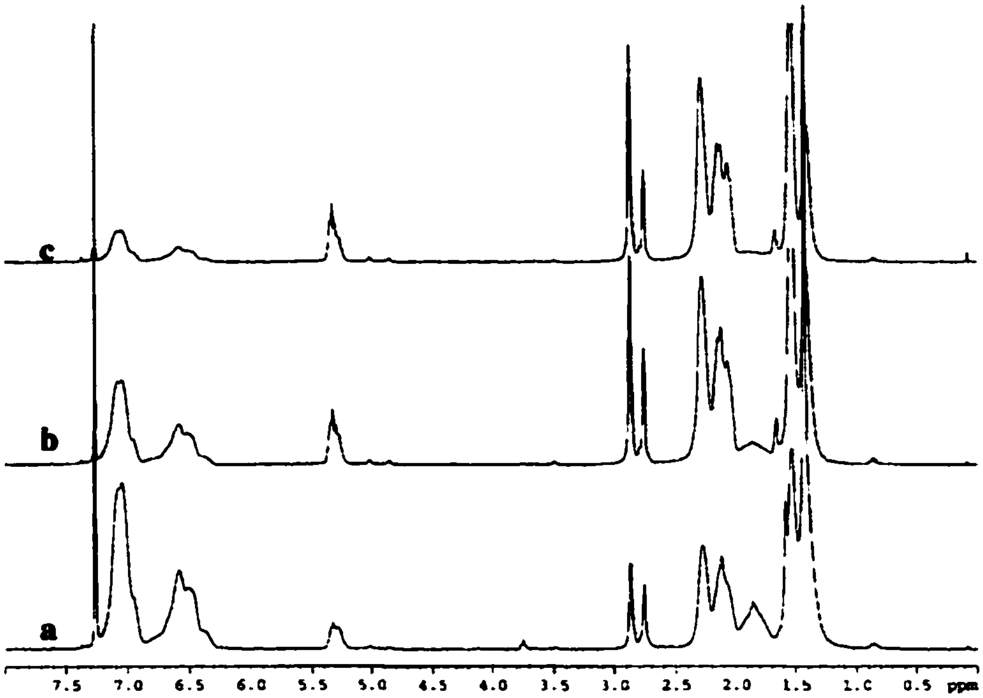


Figure 3.4. ^{1}H NMR of poly(PMB-*b*-styrene) at various incorporations of PMB. (a) 13, 30% PMB, (b) 14, 60% PMB, (c) 15, 80% PMB.

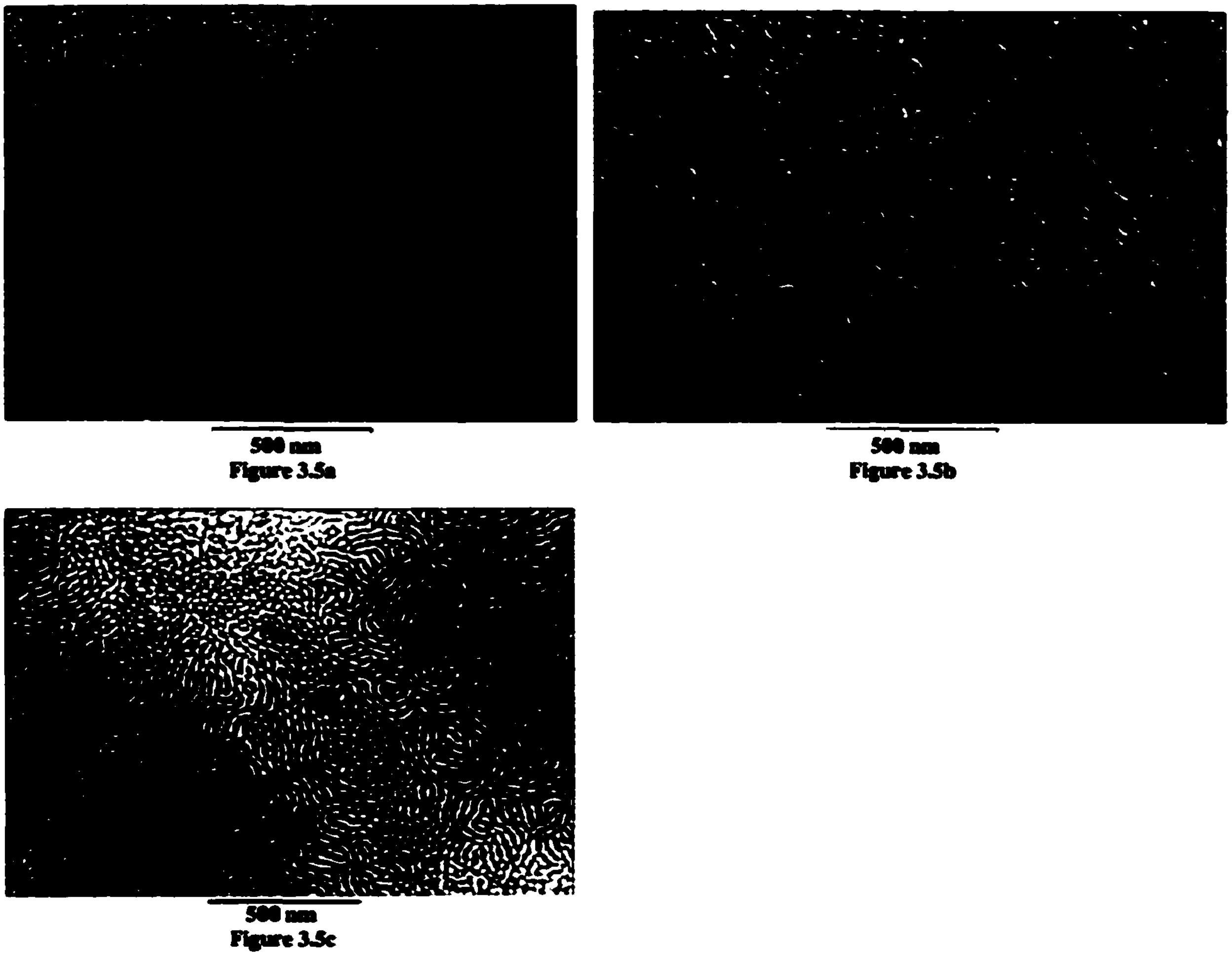


Figure 3.5a

Figure 3.5b

Figure 3.5c

Figure 3.5. TEM of 40.0 x 10^3 g/mol poly(PMB-*b*-styrene). (a) 30% PMB, (b) 60% PMB, (c) 80% PMB.

Figure 3.6a

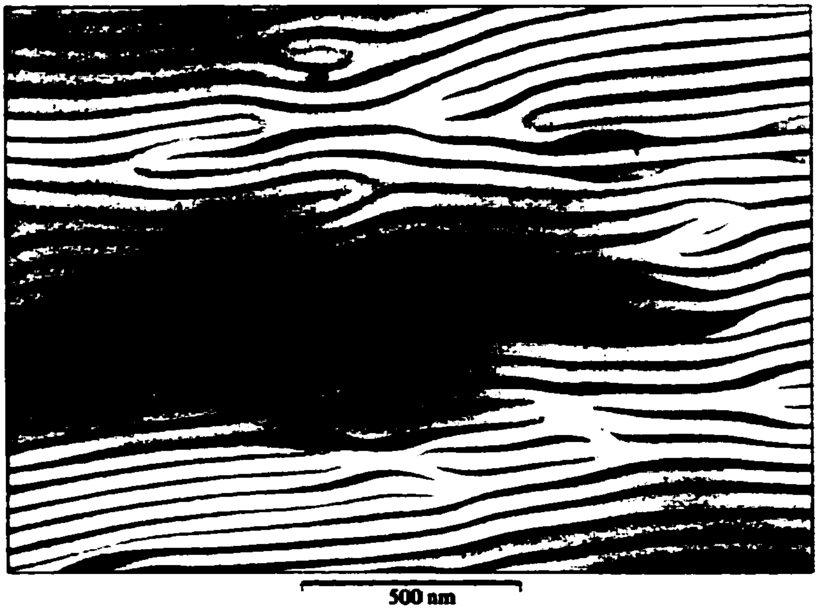


Figure 3.6b

Figure 3.6. TEM of 30.0 x 10^3 g/mol poly(PMB-*b*-styrene). (a) copolymer **9** (b) quaternized copolymer **9**.

CHAPTER 4. A SERIES OF NEW HIGH-PERFORMANCE MATERIALS BASED ON NUCLEOPHILIC AROMATIC SUBSTITUTION OF POLY(4'-FLUOROPHENYL-BIS(4-PHENYL)PHOSPHINE OXIDE)

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Laura A. Rusch-Salazar and Valerie V. Sheares

Abstract

A new series of high-performance poly(arylene phosphine oxide) materials were synthesized post-polymerization from a fluorinated poly(arylene phosphine oxide) (f-PAPO). The new materials had increased solubility and film-forming ability over the parent f-PAPO. With careful choice of nucleophile, thermal stability was also increased. The parent polymer f-PAPO was synthesized via Ni(0) coupling from aromatic chloride and mesylate monomers. Both monomers were polymerized successfully to create polymers with intrinsic viscosities of 0.235 and 0.123 dL/g, respectively. The higher molecular weight f-PAPO gave a glass transition of 320 °C and a char yield of 54% at 650 °C in air. Substitution of f-PAPO via nucleophilic aromatic substitution produced PAPO thermoplastics with significant changes in properties. The largest increase in thermal stability relative to f-PAPO was from 563 to 600 °C 10% weight loss values in nitrogen after displacement of fluoride by 4-aminophenol to give poly(4-(4-aminopheonxyphenyl)bis(4'-phenyl)phosphine oxide). Additionally, the char yield increased from 54 to 71% in air at 650 °C. Solubility of the parent polymer was

improved after substitution using 3-*tert*-butylphenol, *n*-nonylamine and poly(ethylene glycol)monomethyl ether. All of which became soluble in chloroform, DMAc and DMSO.

Copolymers were synthesized using 2,5-dichloro-4'-fluorobenzophenone to improve solubility of f-PAPO without the loss of thermal stability. These copolymers also underwent nucleophilic aromatic substitution to create an epoxy cure agent that was used with D.E.N. 431™ resin.

Introduction

High performance polymers containing phosphine oxide are of great interest due to their increased thermal stability and inherent flame resistance.[1-3] Most of the materials containing the phosphine oxide unit also include other heteroatoms in the backbone weakening the material's structure and overall stability.[2] The first material containing only phosphine oxide and benzene was synthesized by McGrath *et al.*[1] Poly(arylene phosphine oxide) (PAPO) was prepared using Ni(0)-catalyzed coupling of bis(4-chlorophenyl)phenylphosphine oxide. A high glass transition temperature (365 °C) and high char yields were reported in nitrogen and air (35% at 750 °C). Due to the exceptional properties shown by PAPO and the potential for tailoring the material to specific properties, we have applied our methodology for the introduction of functional groups to the polymer backbone through nucleophilic aromatic substitution to the PAPO system. This led to a series of materials with increased thermal stability over PAPO and a remedy to the solubility and film-forming shortfalls of the PAPO system. Nucleophilic aromatic substitution was also used on a copolymer system containing PAPO to synthesize an epoxy thermoset.

Ni(0)-catalyzed coupling has been used to make many substituted poly(*p*-phenylene)s and other materials containing aromatic structures in the backbone.[4-10] The Sheares group has used Ni(0)-catalyst chemistry to synthesize poly(4'-fluoro-2,5-diphenylsulfone) and high molecular weight poly(4'-fluoro-2,5-benzophenone) (PPP).[11-13] Many of the functional groups that are desired in a material often contain sources of hydrogen or functionality that will adversely coordinate with the nickel and ultimately break down the catalyst system. Our approach to functionalizing the polymer after it is synthesized circumvents the need for extensive monomer development and allows for the optimization of one monomer in polymerization instead of alteration of the catalyst system for a series of monomers. The active site along the backbone allows for nucleophilic aromatic substitution (S_NAr) of the final polymer product. The aryl fluoride does not participate in Ni(0)-coupling and is therefore preserved for later use in S_NAr of the final material. Previously it was shown that methyl *p*-fluorophenyl sulfone could undergo S_NAr with primary and secondary amines to give high yields under mild conditions.[14] This same chemistry was applied to the poly(4'-fluoro-2,5-benzophenone) system using post-polymerization S_NAr to produce functionalized PPPs and PPP thermosets. A number of functional groups that were able to undergo S_NAr were used to alter the properties of the material. By this approach, a series of functionalized PPP materials with a range of glass transition temperatures, thermal stabilities and applications were produced from one monomer by simply changing the nucleophile.[12]

Here we describe the synthesis of new functionalized PAPOs containing a reactive site for post-polymerization S_NAr. This approach allows for the increase of molecular weight, variation in properties such as solubility and thermal stability as well as the use of one of the materials as a new thermally stable epoxy cure agent.

Experimental

Materials. All reagents were purchased from Aldrich and used as received unless otherwise stated. *N,N*-dimethylacetamide (DMAc) was stirred over calcium hydride for 24 h and distilled under vacuum. Tetrahydrofuran (THF) was also stirred over calcium hydride for 24 h and distilled under argon. Triphenylphosphine was recrystallized from cyclohexane.

Characterization. All ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) monomer spectra were acquired using a Varian VXR-300. All polymer ^{13}C NMR spectra were acquired using a Bruker AC-200 (50.3 MHz) or a Varian VXR-400 (100 MHz). The ^{19}F NMR spectra were acquired using a Varian VXR-400. Intrinsic viscosity measurements were conducted in DMAc at 30 °C using a Cannon-Ubbelohde viscometer. Thermogravimetric analysis was carried out using a Perkin Elmer TGA 7 with a heating rate of 10 °C/min. Glass transition temperatures were determined using a Perking Elmer Pyris 1 Differential Scanning Calorimeter (DSC) with heating rate of 10 °C/min. The second heat was used for all data. Mechanical testing was performed using three-point bending tests on a dynamic mechanical analyzer (Perkin Elmer DMA7e). Samples were machined into bars approximately 1.5 mm in height by 3 mm in width. They were subjected to a 110 mN static force and 100 mN oscillatory dynamic force (frequency = 1 Hz). The samples were examined at a scan rate of 5 °C/min. The storage modulus (E', Pa) was used to compare the mechanical strength of the materials.

4-(Fluorophenyl)-4',4''-di(hydroxyphenyl)phosphine oxide (1). The synthesis of 1 is described elsewhere.[15]

4-(Fluorophenyl)-4',4''-di(methanesulfonyloxyphenyl)phosphine oxide (2). To a 500 mL round bottom flask, 10 g (30.5 mmol) of compound 1 and 200 mL of pyridine were added and stirred at room temperature until 1 was completely dissolved. Methane sulfonyl chloride (10.6 g, 92.4 mmol) was added drop wise while stirring. The reaction was stirred at room temperature for 16 h. The solution was subsequently added to approximately 400 mL of water and extracted with ethyl acetate twice. Organic layers were combined and dried over magnesium sulfate. Upon evaporation of the solvents (both ethyl acetate and pyridine were removed), a brown oil remained. The crude product was treated with decolorizing carbon in acetone, filtered and evaporated to give a yellow oil. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.15 (s, 6H), 7.12-7.17 (td, 2H), 7.35-7.38 (dd, 4H), 7.58-7.64 (m, 2H), 7.63-7.70 (dd, 4H). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 38.0, 116.4, 122.5, 127.6, 127.7, 130.5, 131.6, 134.0, 134.5, 152.0, 164.1, 166.6.

4-(Fluorophenyl)-4',4''-di(chlorophenyl)phosphine oxide (3). To a 250 mL round bottom flask, 20.3 g (61.0 mmol) dichlorotriphenylphosphorane (Ph_3PCl_2) was added under inert atmosphere. Compound 1 was then added (10.0 g, 30.5 mmol) and the reaction vessel was heated using a sand bath to 350 °C for 4 h or until no more hydrochloric acid was released. The black crude product was dissolved in acetone and treated with decolorizing carbon. After filtration, the acetone was evaporated and the white solid was further purified using column chromatography. Alumina (basic) was used for separation of the product from triphenylphosphine oxide using 1% methanol in ether as eluent. The final pure product is crystalline and white. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14-7.21 (dt, 2H), 7.43-7.49 (m, 4H), 7.52-7.71 (m, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 116.41, 116.62, 129.27, 129.404, 130.16, 131.22, 132.14, 132.37, 133.49, 133.60, 134.61, 134.72, 134.81, 139.26, 164.10, 166.77. High resolution mass spectroscopy: theoretical mass = 363.99869, experimental mass = 363.99908 with a deviation of 1 ppm.

2,5-Dichloro-4'-fluorobenzophenone (6). The synthesis of **6** is described elsewhere.[5]

Polymer Synthesis. To a previously flame-dried 100 mL two-neck, pear-shaped flask, equipped with an overhead stirrer, were added zinc (2.0 g, 30.6 mmol), nickel chloride (0.15 g, 1.16 mmol), and triphenylphosphine (2.0 g, 7.6 mmol). Additions of the catalyst mixture to the reaction flask were made in a dry box under a nitrogen atmosphere. The flask was then sealed with a septum and 3 mL of anhydrous DMAc were added via syringe. The stirred mixture was heated in an oil bath to 80 °C under argon. The catalyst mixture's color changed from yellow-brown to deep green and finally bright red, before addition via syringe of **2** or **3** (**2** or **3** and **6** for the copolymer), dissolved in 2 mL of anhydrous DMAc. The reaction was allowed to proceed for 24 h before precipitation into 40% HCl/methanol to remove zinc. (**4, 5**) ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.41 (2H), 7.73-7.78 (6H), 7.88 (4H). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 115.9, 127.0, 127.7, 129.8, 132.2, 134.3, 142.5, 161.6, 166.9. ^{19}F NMR (DMSO-d_6): δ -100.5 (s, 1F). Elemental analysis: theoretical %C = 73.5% and %H = 4.11, experimental %C = 68.7 and %H = 3.7. (**7, 8**) ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.91-6.99, 7.17-7.22, 7.38-7.88. ^{13}C NMR (50.5 MHz, CDCl$_3$): δ 115.46, 116.02, 116.29, 116.45, 116.71, 127.62, 127.86, 129.38, 130.45, 131.11, 132.83, 133.03, 133.64, 134.59, 134.79, 134.98, 138.78, 143.74, 162.91, 163.24, 168.01, 168.84, 196.23. ^{19}F NMR (CDCl$_3$): δ -100.5 (s, 1F), -99.0 to -98.5 (m, 1F).

Pendent Group Subsitution. *n-Nonylamine* (**9**). Polymer **5** (0.15 g, 0.5 mmol), *n*-nonylamine (0.143 g, 1.0 mmol) and excess anhydrous potassium carbonate (0.32 g, 2.35 mmol) were added to a 25 mL, three-neck, round-bottom flask, equipped with a magnetic stir bar and rubber septum. The glassware was previously flame-dried and kept under a constant flow of argon. DMAc (5 mL) was added to the flask via syringe and the flask was immersed in an oil bath preheated to 130 °C for 24 h. The solution changed from clear to a peach-bronze color during the course of the reaction. The solution was poured into 100 mL of methanol, acidified with HCl to remove K_2CO_3 and was stirred for 2 h. The precipitate was then collected by suction filtration and dried under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (3H), 1.26 (12H), 1.58 (2H), 3.13 (2H), 4.14 (1H), 6.60 (2H), 7.41-7.48 (2H), 7.61-7.81 (8H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 14.30, 22.85, 27.27, 29.44, 29.58, 29.71, 32.04, 40.163, 43.51, 112.01, 112.27, 116.33, 118.58 127.29, 127.53, 128.44, 128.68, 129.12, 131.81, 132.18, 132.38, 132.82, 133.02, 133.79, 134.02, 134.45, 143.37, 151.68. Similar procedures were used for the nucleophilic aromatic substitution of f-PAPO with 4-*tert*-butylphenol, poly(ethylene glycol)monomethylether (repeat unit average = 7), 4-methylbenzylamine, 4-aminophenol, 3-*tert*-butylphenol and *n*-nonylamine with the copolymer (f-PAPO-*co*-PPP).

4-tert-Butylphenol (**10**): ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.24 (9H), 7.03 (4H), 7.40 (2H), 7.65-7.72 (6H), 7.85 (4H).

Poly(ethylene glycol)monomethylether (repeat unit average = 7) (**11**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.34 (3H), 3.53-3.70 (24H), 3.86 (2H), 4.17 (2H), 6.99 (2H), 7.59-7.81 (10H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 59.27, 61.93, 67.76, 69.68, 70.77, 71.06, 72.12, 72.79, 114.90, 115.18, 116.44, 116.71, 127.62, 127.86, 132.84, 133.03, 134.01, 134.24, 134.80, 143.76.

4-Methylbenzylamine **(12)**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.64 (3H), 2.28 (2H), 4.29 (1H), 6.63 (2H), 7.44-7.71 (10H).

3-tert-Butylphenol **(13)**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.27 (9H), 6.85 (1H), 7.03 (2H), 7.20 (1H), 7.62-7.83 (10H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 31.46, 35.07, 117.30, 117.49, 117.62, 117.82, 122.01, 127.45, 127.55, 127.67, 127.76, 129.71, 132.86, 132.96, 134.18, 134.29, 143.59, 154.17, 155.06, 161.79.

4-Aminophenol **(14)**: ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.06 (2H), 6.58 (2H), 6.80 (2H), 6.97 (2H), 7.61-7.87 (10H).

n-Nonylamine **(15)** (copolymer PAPO-*co*-PPP): ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.87 (6H), 1.26 (26H), 1.66 (4H), 3.01 (2H), 3.11 (2H), 4.19 (2H), 6.36 (2H), 6.59-6.62 (2H), 7.40-7.78 (15H). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 14.33, 22.87, 27.30, 29.47, 29.59, 29.73, 32.06, 33.87, 43.50, 111.36, 112.01, 112.27, 126.41, 127.31, 127.55, 128.97, 129.98, 132.28, 132.82, 133.01, 133.79, 134.00, 134.34, 134.61, 143.36, 151.68, 152.51, 195.90.

Thermoset Synthesis (16). Copolymer **15** was used as an epoxy cure agent with Dow D.E.N. 431 Novolac Epoxy Resin. Substituted copolymer **15** was calculated to have an equivalent weight (molecular weight of repeat unit (amine)/number of active hydrogens) of 369. The Dow resin, D.E.N. 431, has an epoxy equivalent weight of 175.5. The D.E.N. 431 (3.0 g) was heated to 70 °C and mixed with 1.0 g of **15** until a homogeneous mixture was achieved. Diethylenetriamine was then added for the remaining N-H equivalents. The mixture was placed into a die mold to cure at room temperature for 24 h. The material was further cured at 90 °C for 3 h and 130 °C for an additional 3 h. The final cured thermoset was machined into DMA test samples. When **15** was mixed with the warm resin, the mixture appeared miscible and was yellow in color.

Results and Discussion

Monomer Synthesis. The unique physical properties of PAPO led us to the synthesis of monomer **2**. Compound **1** is a white powder and was prepared using the synthesis described by Lin and Long.[15] This compound was only soluble in polar solvents (including pyridine) allowing the replacement of the hydroxyl groups by the methanesulfonyloxy group in basic solution. The product was a sticky, yellow oil after purification. The structure of monomer **2** was verified using ^{1}H, ^{13}C NMR and NOESY. An additional monomer (**3**) was synthesized to investigate the difference in reactivity of the mesylate versus the chloro compound in Ni(0)-catalyzed polymerization. Monomer **3** (4-fluorophenyl-4',4''-di(chlorophenyl)phosphine oxide) was synthesized using **1** and treating it with dichlorotriphenylphosophorane at 350 °C for 4 h (**Scheme 4.1**). Monomer **3** was more difficult to purify due to its close resemblance to triphenylphosphine oxide, the byproduct from the chlorination reaction. Pure product was achieved using column chromatography after treatment with activated carbon in 30% yield. 4-Fluorophenyl-4',4''-di(chlorophenyl)phosphine oxide (**3**) formed white crystals after purification. It should be noted that fluorinated aromatics do not participate in Ni(0)-catalytic aryl-aryl coupling. This was further confirmed for this system when 4,4',4''-tri(fiuorophenyl)phosphine oxide was subjected to Ni(0)-coupling conditions. After the normal reaction time (24 h), the 4,4',4''-tri(fluorophenyl)phosphine oxide was recovered and no polymer was formed.

Polymer Synthesis. Monomers **2** and **3** were used with Ni(0)-coupling to synthesize poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (f-PAPO) in DMAc according to **Scheme 4.2**. Due to the solvent resistance of the material, GPC was not taken. Intrinsic viscosity studies were measured in DMAc at 30 °C and showed the [η] (intrinsic viscosity) was less for the polymer made from monomer **2** (**4**, [η] = 0.123 dL/g) than for the polymer synthesized from monomer **3** (**5**, [η] = 0.235 dL/g). Both polymerizations appeared to behave similarly while in progress. The reaction appeared very dark and viscous after only one hour. After 24 h at 80 °C, the viscous polymerization mixture was poured into HCl/methanol to precipitate the polymer and oxidize any remaining zinc.

The thermal properties increased with molecular weight and are summarized in **Table 4.1**. The T_g of **4** was found to be 305 °C where the T_g of **5** was found to be higher at 320 °C. The 10% weight loss from the TGA was found to increase from 544 to 563 °C under nitrogen and from 537 to 567 °C under air for polymers **4** and **5**, respectively. The char yield at 650 °C also increased 14 wt. % under nitrogen going from 47% for **4** to 61% for **5** and only falling to 59% when **5** was heated to 700 °C. This material (**5**) has higher thermal stability than the non-fluorinated version synthesized earlier (char yield at 650 °C was 45 wt. % under nitrogen).[1]

The appearances of the two materials (**4** and **5**) were also different. Polymer **4** was a tan flaky material while polymer **5** was white and very hard. Both polymers possessed good solvent resistance and were soluble only in DMAc and DMSO, but not in less polar solvents such as $CHCl_3$ or THF. Similar solvent resistance behavior was seen by McGrath with the non-fluorinated material.[1]

This new material (**5**) shows promise for use in high temperature applications because of its high thermal stability and char yield. To examine the thermal stability further, isothermal TGA studies were done on material **5**. No weight loss was seen after 24 h at 300

°C under air. When a sample of **5** was maintained at 400 °C for 24 h under air, an average weight loss of 0.78% per hour was seen.

Earlier, the viscosity data was discussed and it showed that polymer **5** had higher molecular weight than polymer **4**. This was reconfirmed by the increase in the thermal data between the two materials. The aromatic chloride monomer **3** performs better under Ni(0)-catalyzed polymerization conditions leading to higher molecular weight material. Thus, polymer **5** was used for the nucleophilic aromatic substitution reactions.

Polymer Substitution. It has been shown recently that poly(4'-fluoro-2,5-diphenyl sulfone)[4] and poly(4'-fluoro-2,5-benzophenone)[5] could undergo nucleophilic aromatic substitution with a variety of nucleophiles with near quantitative yields. Like carbonyl and sulfonyl groups, phosphine oxide is a good electron-withdrawing group facilitating the S_NAr reaction along the polymer backbone.

Nucleophilic aromatic substitution was carried out on **5** using *n*-nonylamine, 4-*tert*-butylphenol, poly(ethylene glycol)monomethyl ether (PEG), 4-methylbenzylamine, 4-aminophenol and 3-*tert*-butylphenol as the nucleophiles according to **Scheme 4.2**. In all cases, the reaction was carried out in DMAc at 130 °C for 24 h. A 100% excess of nucleophile was used to help drive the nucleophilic substitution. All remaining nucleophile was easily removed when the polymer was precipitated in methanol. The degree of substitution of all the materials (**9**-**14**) could be calculated using the integration from the ^1H NMR and are reported in **Table 4.1**. In the cases of **9**-**13**, the integration values of the aromatic and aliphatic regions were compared. The final material, **14**, was calculated using the protons on the amine compared to the aromatic protons. The near quantitative substitution (99%) of **5** with *n*-nonylamine yielding **9** is more easily demonstrated by the ^{13}C

NMR (**Figure 4.1**). This is evidenced by the disappearance of the doublet at 165 ppm (C-F, **Figure 4.1**, a) in the spectrum of **5** and the appearance of a new peak at 152 ppm (C-N, **Figure 4.1**, b) in the NMR of **9**. Material **11** has only 45% substitution due to the poor nucleophilicity and reactivity of the alkyl alcohol on the PEG. Polymers **12** and **14** had 30 and 60% substitution, respectively, presumably due to the increased solvent resistance and partial precipitation of the material after incomplete substitution.

Polymer Solubility. Polymers **9** and **11** had increased solubility over the parent polymer **5**, presumably due to the flexibility and solvation of the alkyl portions added as the nucleophile. Both polymers were soluble in $CHCl_3$, but not in THF. Polymer **11** also gave flexible, creasable films compared to the brittle films formed from **5**. The 3-*tert*-butylphenol substituted polymer (**13**) also had increased solubility over polymer **5**. Material **13** was soluble in DMSO, DMAc and partially soluble in $CHCl_3$. The material containing the 4-*tert*-butylphenol (**10**) and that containing the 4-aminophenol (**14**) had decreased solubility and were mostly soluble in DMAc, but only partially soluble in DMSO. All materials were white powders except for **14** which was a dark purple color. The intense color given by **14** is presumably due to the chromophore now present with the phenyl side chain in conjugation with the 4-aminophenoxy pendant group.

Thermal Analysis. Another property altered by the nucleophilic substitution is the thermal stability of the materials. The thermal data for these materials are summarized in **Table 4.1**. As expected, all substituted polymers have lower glass transition temperatures than the parent material, **5**. The T_g decreased when more flexible or bulky groups were incorporated into the material. Due to the oxygen or nitrogen used as the nucleophiles, the new bond is now a weaker, more flexible, heteroatom–carbon bond. This leads to lower glass transition temperatures and often lower degradation temperatures especially if the nucleophile used had a long alkyl component.

Differential scanning calorimetry (DSC) was used to measure the glass transition temperatures of the materials. In all cases, the second heat was used. The long alkyl chain present in *n*-nonylamine gives a material with a lower transition temperature than the parent polymer, as expected.[12] The decrease was 145 °C from **5** to **9**. When PEG was used as the nucleophile (**11**) the T_g decreased nearly 170 °C from that of f-PAPO. This too was expected because PEG has a sub-ambient glass transition, but was used as a nucleophile to increase solubility. When *tert*-butylphenol was used as the nucleophile, the glass transition temperature was lower for the 3-substituted phenol (**13**) than for the 4-substituted *tert*-butylphenol (**10**). The *tert*-butyl group was presumed to add some free volume to the system decreasing the glass transition compared to **5**, but the 4-substituted phenol polymer (**10**) was thought to pack better than the 3-substituted version which gave a slightly higher T_g than that for the 3-substituted phenol (241 °C versus 224 °C). The last two materials contained aromatic amines. In one case the amine was attached to the backbone (**12**) and in the other case it was the pendant group (**14**). The higher T_g given by polymer **14** was due to the hydrogen bonding taking place between the primary pendant amines as well as the lack of the methylene that was present in polymer **12**. The amine in polymer **12** was more restricted due to its proximity to the backbone and has more difficulty hydrogen bonding. The one less hydrogen available for intermolecular interaction and the flexibility the methylene unit adds to the free volume contributed to the lower T_g. Although all the glass transitions were lower than the parent polymer, many (**10**, **12**, **13** and **14**) were still very high (>220 °C) compared to industrial high-performance materials. Moreover, these new substituted PAPO materials were functionalized and have solubility and film-forming ability not found in the unsubstituted parent PAPO.

The thermal stability of the materials was tested using thermal gravimetric analysis (TGA) at 10 °C/min. In most cases the 10% weight loss was lower than the 10% weight loss of polymer **5**. This was due to the new, weaker heteroatom–carbon bond formed during nucleophilic aromatic substitution. Only in the case of the *p*-aminophenol substituted polymer **14** was the 10% weight loss greater than that of the starting polymer. Polymer **14** had an increase in the 10% weight loss from 563 °C (**5**) to 600 °C (**14**) in nitrogen and from 567 °C to 588 °C in air. The char yield for **14** was also higher than that seen for polymer **5**. It increases from 61 (**5**) to 66 (**14**) wt. % in nitrogen and from 54 to 71 wt. % in air at 650 °C. Polymer **10** also showed an increase in char yield from 61 (**5**) to 65 (**14**) wt. % in nitrogen at 650 °C and remained nearly the same as **5** in air. In polymers **10** and **14** this increase in char yield was due to the increase in molecular weight upon addition of the nucleophile as well as the addition of a thermally stable moiety. The thermal scans of **5** and **14** are shown in **Figure 4.2.** By the TGA it can also be seen that the degradation reached a plateau near 650 °C and the char yield remained about the same at 700 °C. These materials also had greater stability in air compared to most high-performance materials that degrade quickly in air at these temperatures. Another significant factor of the thermal stability of these materials (besides being highly aromatic) is the mechanism at which the PAPO breaks down at high temperatures, especially in air. The weakest bond in this system was the phosphorus–carbon bonds which break first. The phosphorus then forms a layer of phosphine oxide which prevents oxygen from further penetration and degradation of the material. This was demonstrated by McGrath *et al.* with materials that contained phosphine oxide in the backbone.[3]

Copolymer Synthesis. Due to the good solvent resistance of f-PAPO and many of the substituted polymers which could lead to difficult processing, copolymers were investigated. The second monomer used (**6**) for the copolymer was chosen due to its good homopolymer properties. The homopolymer of **6** is poly(4'-fluoro-2,5-benzophenone) (PPP) and was soluble in common organic solvents such as THF and $CHCl_3$. PPP also had good thermal properties with a T_g at 167 °C and 10% wt. loss at 566 and 611 °C in air and nitrogen, respectively.[5] Monomer **6** also contained an active site for nucleophilic aromatic substitution. The copolymer was expected to have better solubility than f-PAPO and good although decreased thermal stability due to the PPP incorporation. Copolymers were synthesized much the same way as f-PAPO. Ni(0)-catalyzed coupling was used to combine the two monomers and synthesize a random copolymer that was white in color. The copolymer was made using either monomer **2** or **3** as the PAPO monomer and compound **6** as the benzophenone monomer according to **Scheme 4.3**. It was found that a higher molecular weight could be achieved using the dichloro monomer **3** instead of the mesylate monomer **2**. The number average molecular weight ($\langle M_n \rangle$) of the PAPO-*co*-PPP made with **2** and **6** (**7**) was 4.6 x 10^3 g/mol with a PDI of 1.9 and that made with **3** and **6** (**8**) yielded a polymer with a $\langle M_n \rangle$ of 5.9 x 10^3 g/mol with a PDI of 2.5. Polymer **7** was readily soluble in THF so molecular weight data could be acquired using GPC. Polymer **8** was not soluble in THF, but was soluble in chloroform after it was purified by Soxhlet extraction and a GPC was taken in chloroform. The compositions of the two polymers were also different. Since the mesylate PAPO monomer was less reactive toward Ni(0) coupling than the benzophenone monomer, the feed ratio of 1:1 yielded a polymer with incorporation of PAPO to PPP of 11:89. This explains why this material was soluble in THF because it was more like the PPP which as a homopolymer has much better solubility than PAPO. The polymer made using the dichloro monomer with **6** had a feed ratio of 1:1 and an incorporation of 43% PAPO and 57% PPP. The incorporation of the two units into the polymer was calculated using the integration from the ^{19}F NMR. Due to almost equivalent incorporation of both monomers, this copolymer possessed the properties of both polymers which was seen by its increased solvent resistance over PPP.

The difference in the composition of the two materials was also evidenced upon examination of the thermal data. As expected, the polymer with higher molecular weight and higher PAPO content had much higher thermal stability and a higher glass transition temperature. The data for the copolymers are summarized in **Table 4.2**. The 10% weight loss for **7** was 559 °C in nitrogen and 535 °C in air. For polymer **8**, the 10% weight loss in nitrogen was 583 °C and in air was 552 °C, a significant improvement over **7**. When the benzophenone monomer is polymerized to a homopolymer, there was always a significant amount of reduction of the ketone to a secondary alcohol. This reduction was not seen with the copolymerization. The ^{19}F NMR in **Figure 4.3** shows two peaks representing the two types of fluorine that are present. The first peak at -100.5 ppm (**Figure 4.3**, a) represents the fluorine from the PAPO portion of the copolymer and the second peak at -98.5 to -99.0 ppm (**Figure 4.3**, b) represents the fluorine in the PPP portion. The ^{19}F NMR of the PPP homopolymer showed a peak at -109.0 ppm representing the units containing the secondary alcohol,[5] this peak was not seen in the copolymer ^{19}F NMR. The lack of reduction was presumably due to the presence of the phosphine oxide. This was further investigated by running a polymerization of 2,5-dichloro-4'-fluorobenzophenone in the presence of triphenylphosphine oxide. The polymer had only 4% reduction of the ketone compared to the 22% reduction when triphenylphosphine oxide was not added.[12]

Copolymer Substitution. Both units of the copolymer contained an aromatic fluorine that could be used in nucleophilic aromatic substitution. Polymer **8** underwent S_NAr using the same conditions as were used for homopolymer **5**. The nucleophile used with the copolymer was *n*-nonylamine to produce a substituted polymer that could be used later as an epoxy cure agent. The substitution proceeded in 99% yield to give a yellow polymer powder (**15**). The thermal data were decreased from that seen with the parent PAPO-PPP as expected and are summarized in **Table 4.2**. The glass transition temperature decreased to 163 °C from 287 °C for the unsubstituted polymer. The thermal stability was also decreased due to the addition of the alkyl group with a drop to 45 wt. % in the char yield at 650 °C under nitrigen.

Thermosets. Polymer **15** was used as the cure agent with an epoxy. The secondary amine was used to cure the epoxy moiety causing a crosslinked network that was completely insoluble in any common organic solvents. The thermoset was made by mixing **15** with Dow liquid novolac epoxy D.E.N. 431™ resin in a ratio of 1.0 g of substituted PAPO-PPP with 3.0 g of epoxy resin. The amount of resin used was based on the amount needed to fully dissolve the PAPO-PPP cure agent powder instead of the epoxy/amine equivalent weight. As is often the case, the remaining epoxy equivalent weight was cured using a small molecule cure agent, diethylenetriamine. The D.E.N. 431™ and **15** were mixed at 70 °C. Once **15** completely dissolved in the resin the diethylenetriamine was added and the mixture was poured into a mold and allowed to cure at room temperature for 24 h. The thermoset was then heated to 90 °C for three h and then 130 °C for an additional three hours. The thermoset was yellow in color and appeared to be homogeneous. An increase of 4.0 GPa in the storage modulus was seen in the DMA of the thermoset samples made with PAPO-PPP cure agent compared to the neat samples using only D.E.N. 431^{TM} and diethylenetriamine. The use of the PAPO-PPP substituted polymer as the cure agent is an example of how this could be used in high temperature applications where a more thermally stable thermoset is needed.

Conclusion

Poly(arylene phosphine oxide)s were synthesized using two different monomers. Both yielded a polymer with an active site that could be used for nucleophilic aromatic substitution. The polymer made with the dichloro monomer **3** gave higher molecular weight as evidenced by a higher intrinsic viscosity and increased thermal properties. A variety of nucleophiles were chosen to create a series of materials with differing solubility and thermal properties. The advantage of post-polymerization functionalization is the ability to synthesize many materials from one monomer and the optimization of the Ni(0)-catalyzed coupling polymerization of that monomer. The differences in the physical properties of the derivatives was similar to those observed from substitution of poly(4'-fluoro-2,5-benzophenone). The thermooxidative stability of the unsubstituted polymer and those that were substituted were very high compared to most high-performance materials due to the incorporation of the phosphine oxide into the polymer backbone.

Copolymers could also be made using 2,5-dichloro-4'-fluorobenzophenone and monomer **2** or **3**. The copolymer made using **3** had increased thermal stability due to the higher molecular weight and increased incorporation of PAPO units. The copolymer, like the homopolymer, could undergo nucleophilic aromatic substitution to create a secondary amine that was used as an epoxy cure agent. The thermoset made from this substituted copolymer and D.E.N. 431™ had an increased storage modulus over the neat sample.

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Table 4.1. Percent Substitution and Thermal Properties of Substituted f-PAPO.

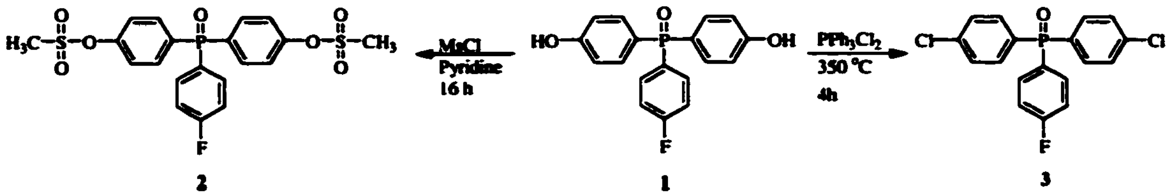
Sample	Substitution, % (by ^{1}H NMR)	T_g (°C)^a	TGA Results (Weight Loss)^b			
			10%, N_2	10%, Air	Char, N_2	Char, Air
4		305	544	537	47	46
5		320	563	567	61	54
9	99	175	484	488	37	25
10	70	241	482	471	65	55
11	45	154	510	517	39	43
12	30	247	535	506	52	40
13	85	224	519	503	37	43
14	60	316	600	588	66	71

[a] Determined by DSC using the second heat at 10 °C/min. [b] Determined by TGA at 10 °C/min, percent char yields are reported at 650 °C.

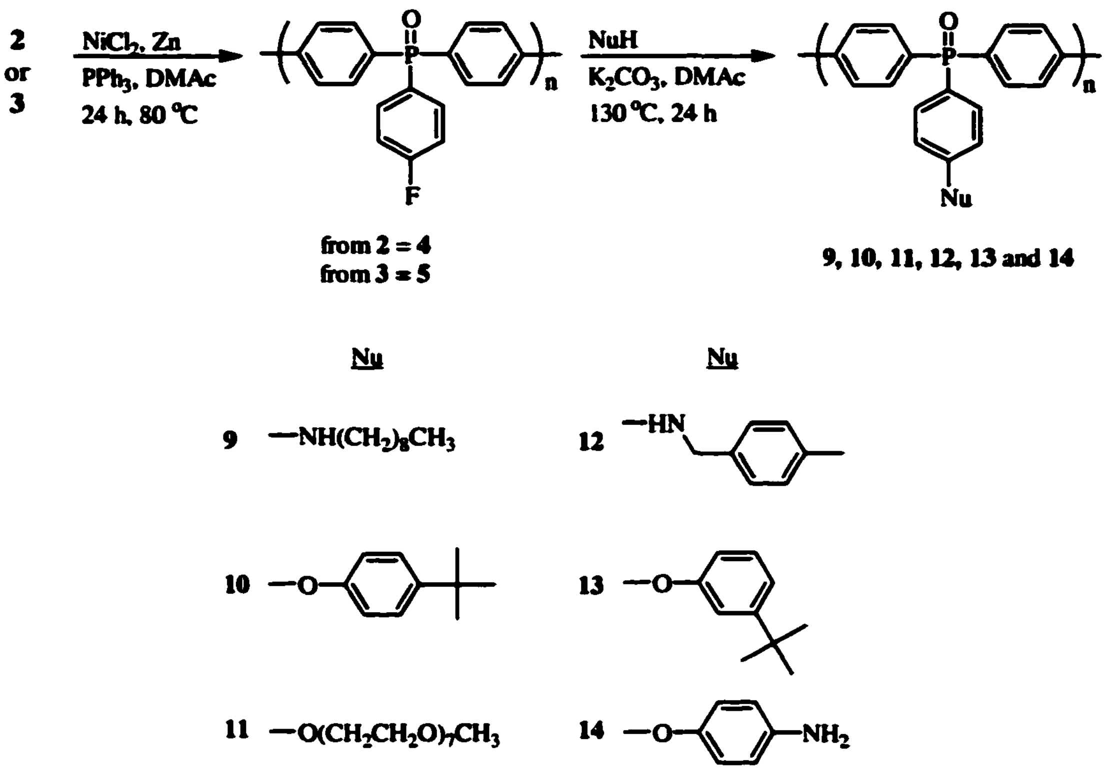
Table 4.2. Copolymer Molecular Weight and Thermal Data.

Sample	<Mn> x 10^{-3} g/mol[a]	PDI	T_g (°C)[d]	TGA Results (Weight Loss)[e]			
				10%, N_2	10%, Air	Char, N_2	Char, Air
7	4.7[b]	1.9	152	559	535	66	51
8	5.9[c]	2.5	287	583	552	69	53
15			163	465	416	45	46

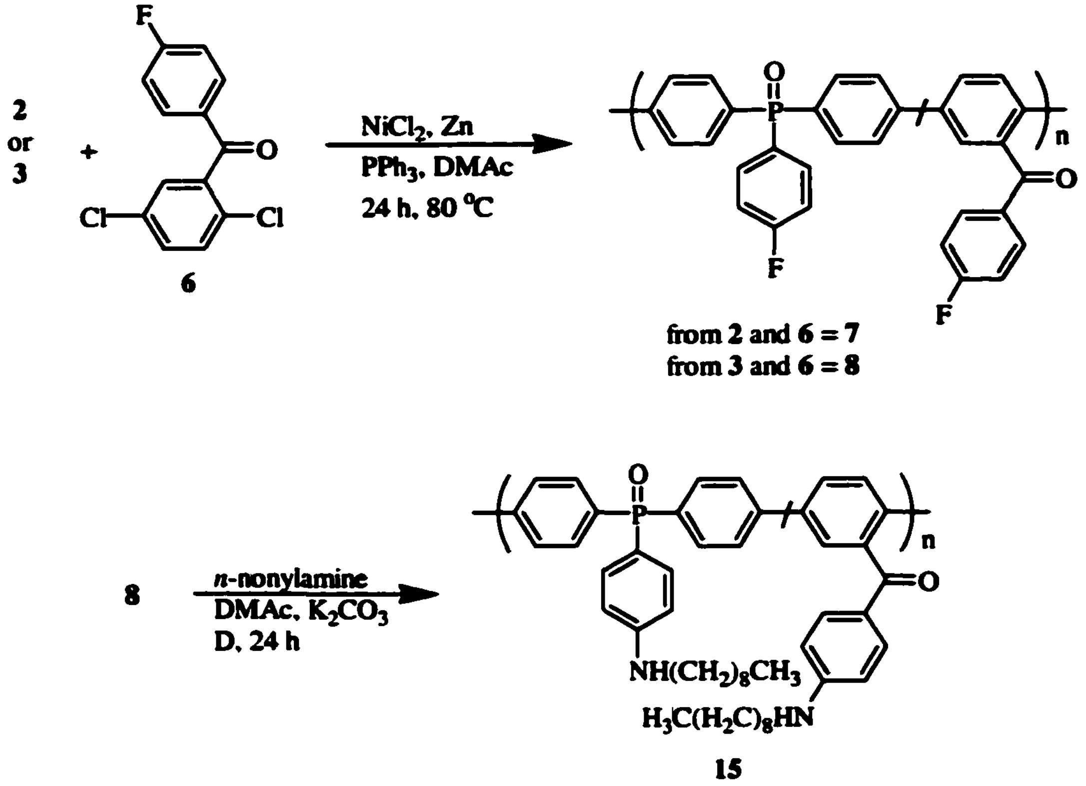
[a]Determined by GPC using polystyrene standards. [b]GPC run in THF. [c]GPC run in chloroform. [d]Determined by DSC using the second heat at 10 °C/min. [e]Determined by TGA at 10 °C/min, percent char yields are reported at 650 °C.



Scheme 4.1. Synthesis of 4-(fluorophenyl)-4',4''-di(methanesulfonyloxyphenyl) phosphine oxide (2) and 4-(fluorophenyl)-4',4''-di(chlorophenyl)phosphine oxide (3).



Scheme 4.2. Synthesis of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (f-PAPO) (4, 5) and nucleophilic aromatic substitution with various nucleophiles.



Scheme 4.3. Copolymer synthesis and nucleophilic aromatic substitution with *n*-nonylamine.

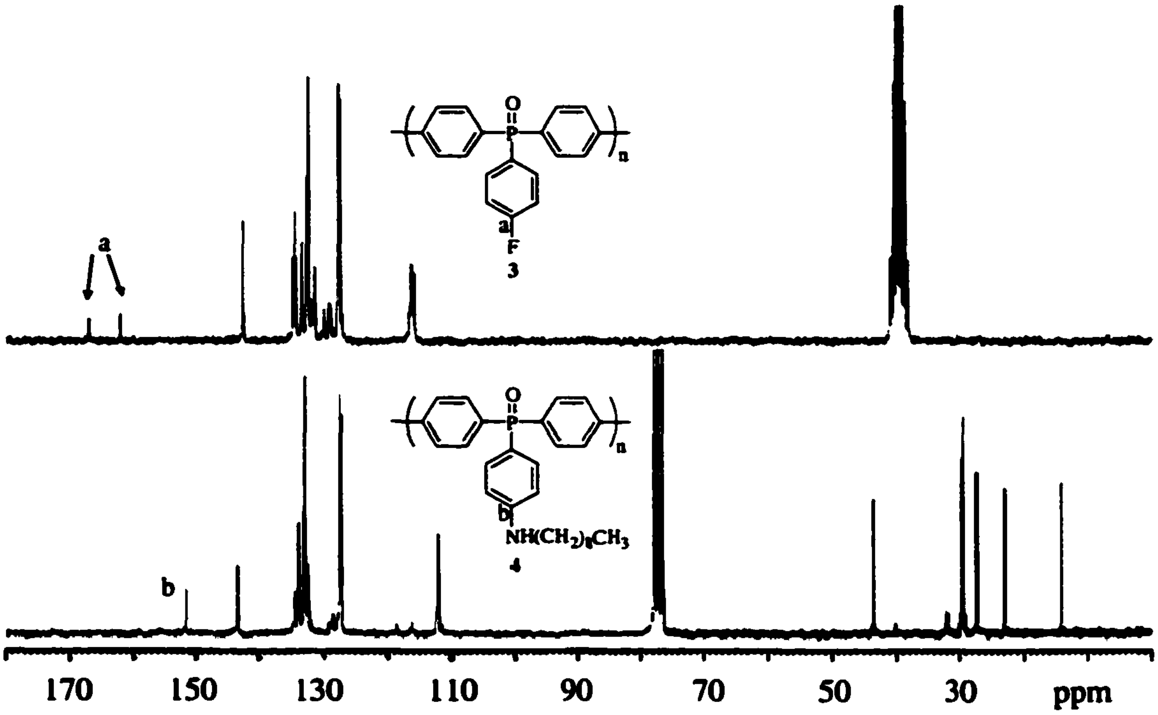


Figure 4.1. ^{13}C NMR of f-PAPO and *n*-nonylamine substituted PAPO.

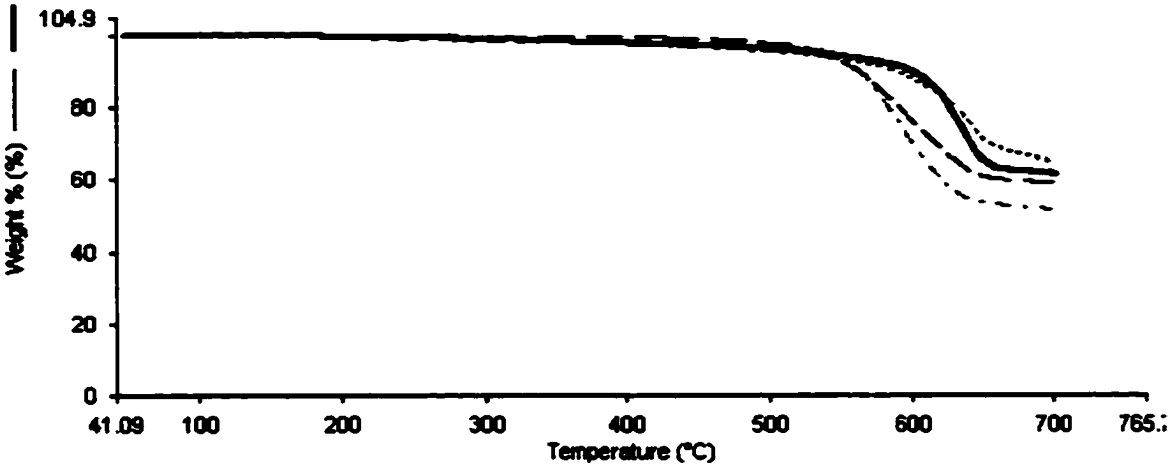


Figure 4.2. TGA traces at 10 °C/min of f-PAPO, **5**, and **14**. – · – · **5** under air, – – – **5** under N_2, ······ **14** under air, —— **14** under N_2.

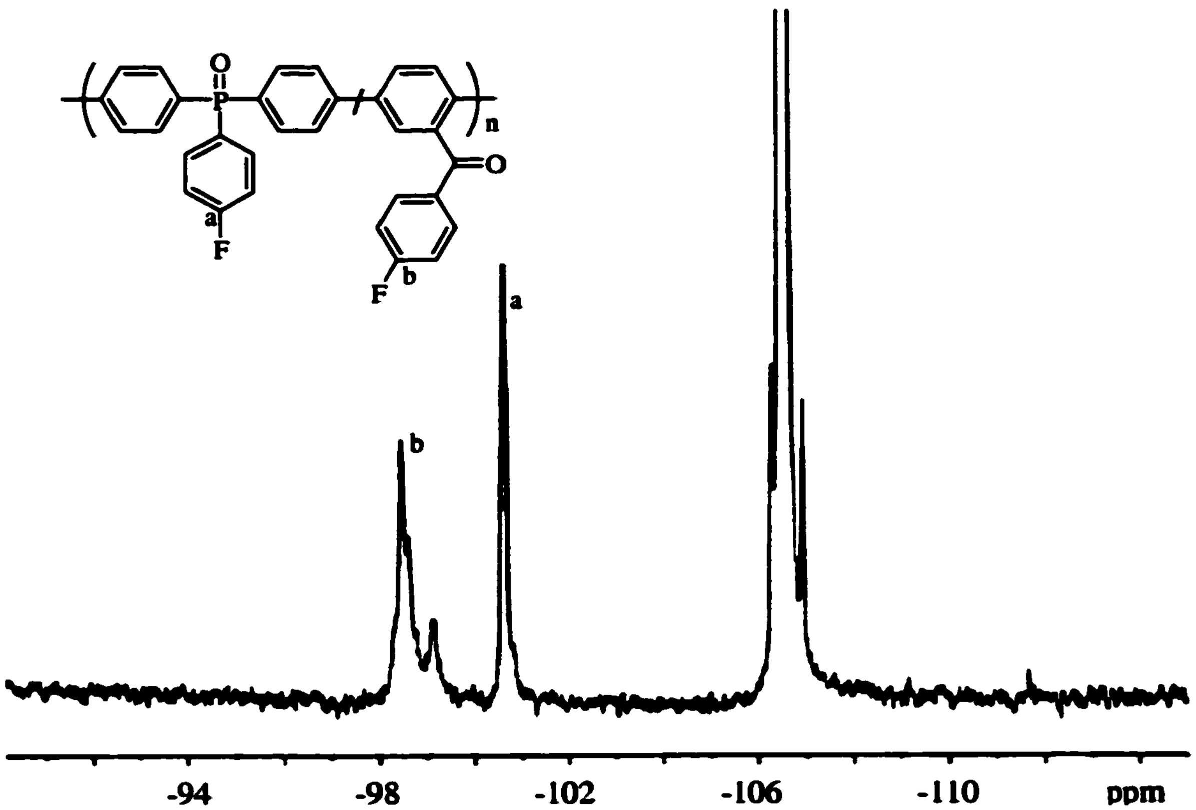


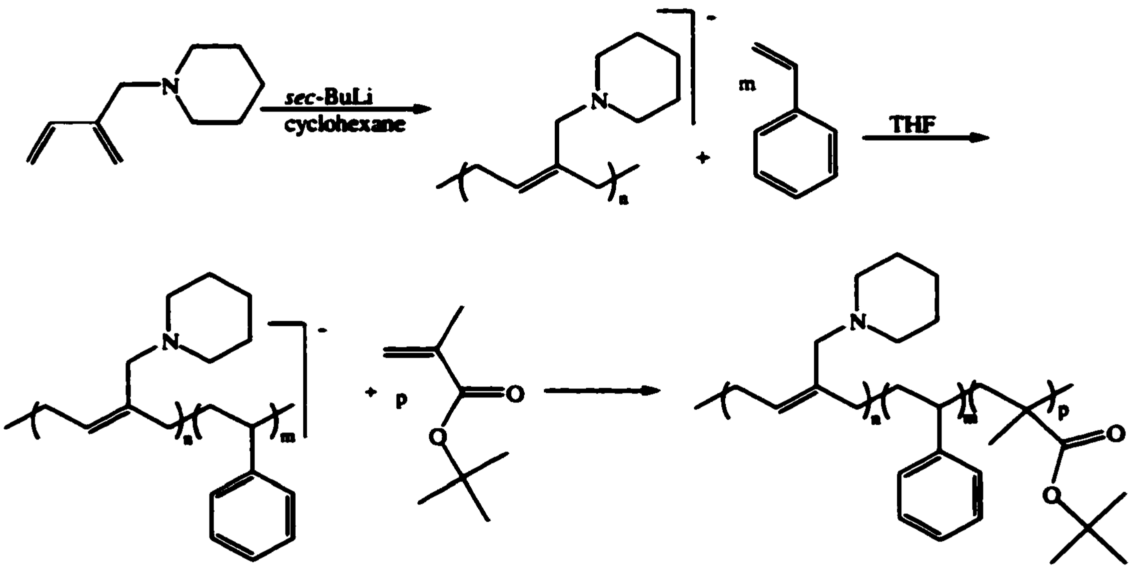
Figure 4.3. ^{19}F NMR of copolymer 8 (fluorobenzene added as reference, -106.5 ppm).

CHAPTER 5. GENERAL CONCLUSIONS

Functionalized materials offer many advantages over their unsubstituted counterparts. This dissertation focused on the options for polymer functionalization. The first approach is to add the desired moieties onto the monomer before polymerization, where the second route utilizes post-polymerization reactions to alter the material. Both methods were discussed in detail within this dissertation.

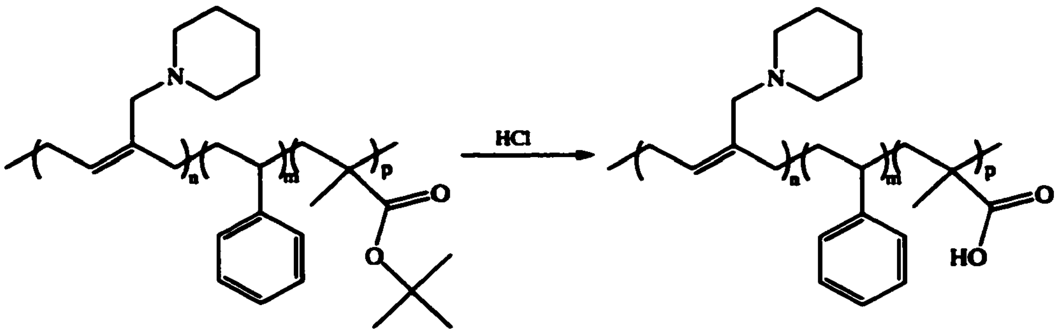
The first approach was used to make the new materials discussed in chapters two and three. The amine functionality was chosen for substitution because of its great versatility and potential for applications. The monomer, 2-(*N,N*-piperidylmethyl)-1,3-butadiene (PMB), was polymerized using bulk and emulsion free radical techniques as well as anionic methods. In the free radical case, random copolymers with styrene were also synthesized to show how this monomer could be used to synthesize functionalized styrene butadiene rubber. Our anionic polymerization approach is also advantageous because it allows for control over the molecular weights as well as the synthesis of block copolymers. In chapter 3, block copolymers with PMB and styrene were investigated. These materials were used to demonstrate their potential in lithography by investigating their use with electroless plating. The block copolymers also have the possibility of being used as surfactants, sealants, compatiblizers, etc. The homopolymer and its ability to become water soluble upon quaternization was also of explored. It would be advantageous to investigate even higher molecular weights than what had been achieved herein as well as the use of amine groups other than the piperidyl moiety to alter the glass transition temperature and other properties.

Triblock copolymers are of great interest for phase separation studies and industrial applications. Depending on the monomers chosen, the materials could have greater water solubility or complex solubility that depended on pH, temperature and electrolyte concentration. One example of a triblock copolymer is seen in **Scheme 5.1**. The monomers shown are PMB, styrene and *tert*-butylmethacrylate (*t*BMA).



Scheme 5.1. Tribolock copolymers containing PMB, styrene and *tert*-butylmethacrylate.

The third block chosen, *t*BMA, could be easily hydrolyzed to methacrylic acid as shown in **Scheme 5.2**. This polymer would then have complex solution properties and interesting phase separation. Along with conversion to the acid, the polymer still has the possibility to be quaternized. If the amine is quaternized the material would behave as a polyelectrolyte until the pH was sufficiently high to remove all of the protons off the acid units and the material then would be a copolyampholyte (if the amine and acid monomers



Scheme 5.2. Hydrolysis of *t*BMA to methacrylic acid.

were incorporated in equal amounts). Phase separation studies of the quaternized and unquaternized versions would also be interesting to see how the charged blocks interact.

Another series to be investigated is that of thermoplastic elastomers. These materials are of interest because they perform like a crosslinked elastomers but the crosslinks are physical instead of chemical. This physical interaction allows the polymer to be reused or reset by taking it above the T_g of the end blocks or by dissolving it into solution. To synthesize thermoplastic elastomers, a diinitiator must be used and the middle block needs to have a glass transition below 0 °C (rubbery) while the end blocks must be glassy. Any of the symmetric 2-(*N,N*-dialkylaminomethyl)-1,3-butadienes already investigated would be useful as the middle block – the rubber. The diethyl or dipropyl amines lend themselves well to be the middle block because their glass transitions are well below ambient temperatures.

The second approach to functionalization, post-polymerization, was investigated for poly(arylene phosphine oxide)s (PAPO). The PAPO materials discussed in chapter 4 are inherently flame resistant due to the phosphine oxide in the backbone. After polymerization of the monomer, nucleophilic aromatic substitution was utilized to create a series of high performance materials that had altered properties. When synthesizing the monomer, one of the steps involves a Gringnard reaction. This step allows for the use of many other Grignard reagents and could be used to extend the properties of these types of materials even further. The only consideration is the stability of the new pendant group to the Ni(0)-catalyzed coupling reaction that is used in the polymerization.

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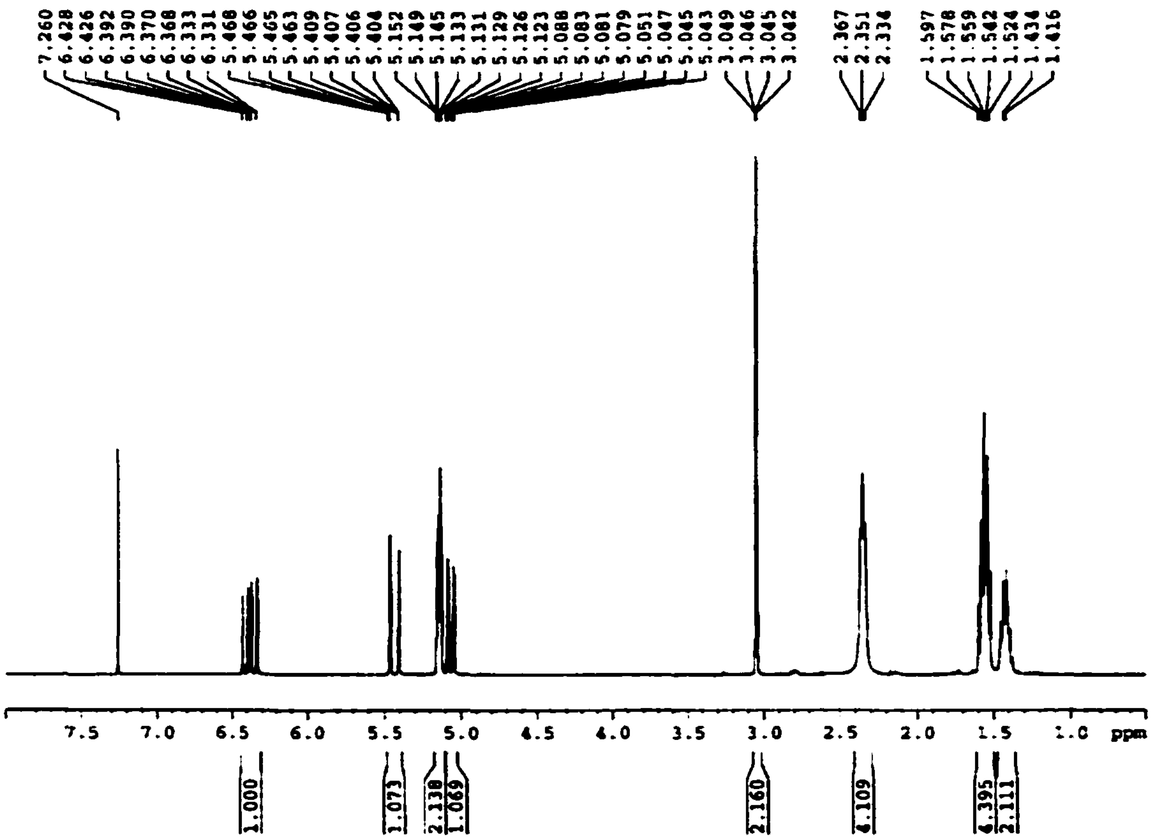
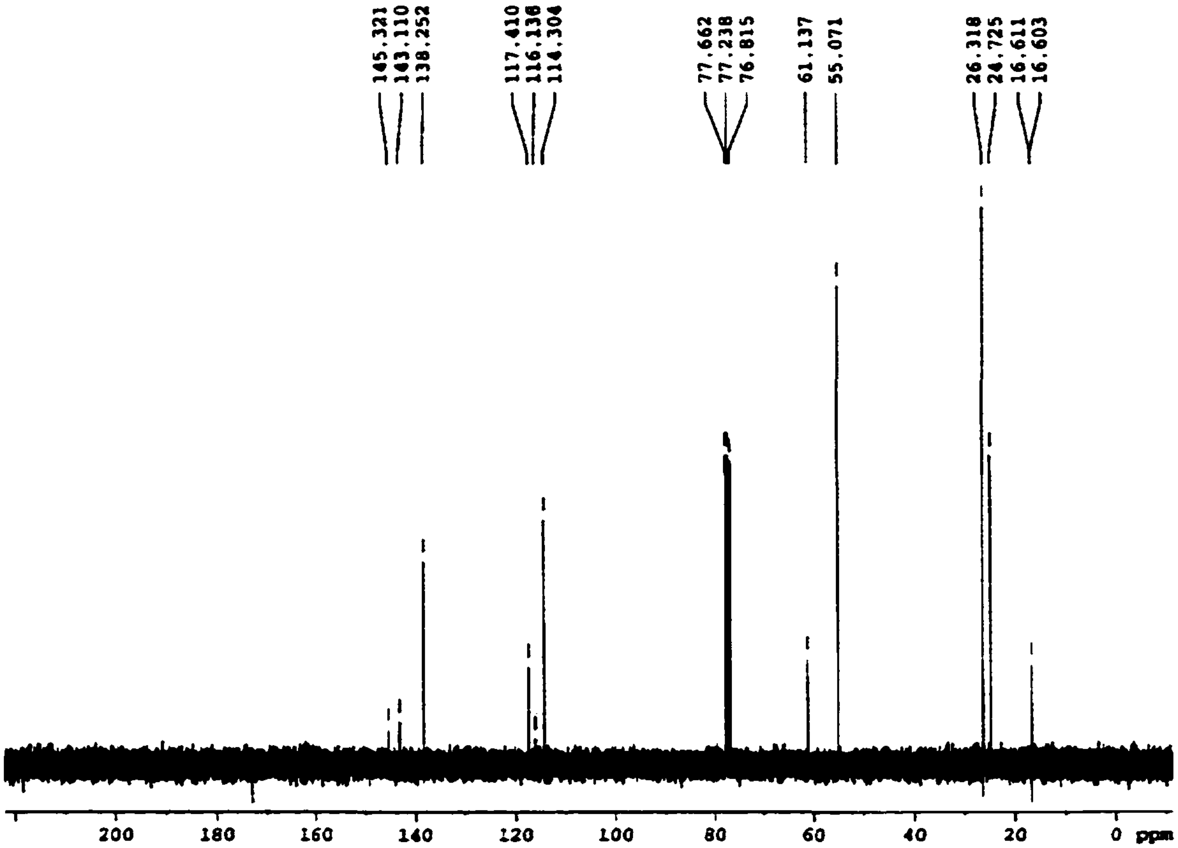
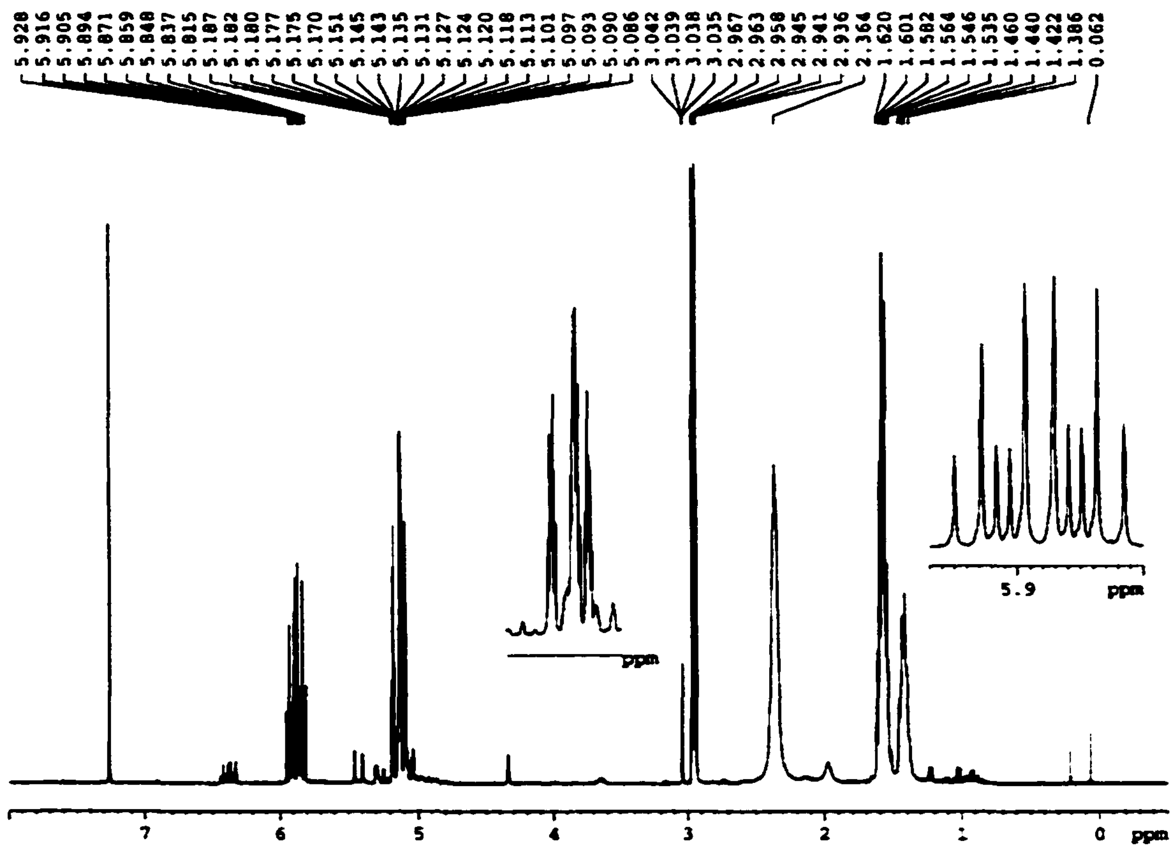
APPENDIX A. SUPPEMENTAL DATA FOR CHAPTER 2



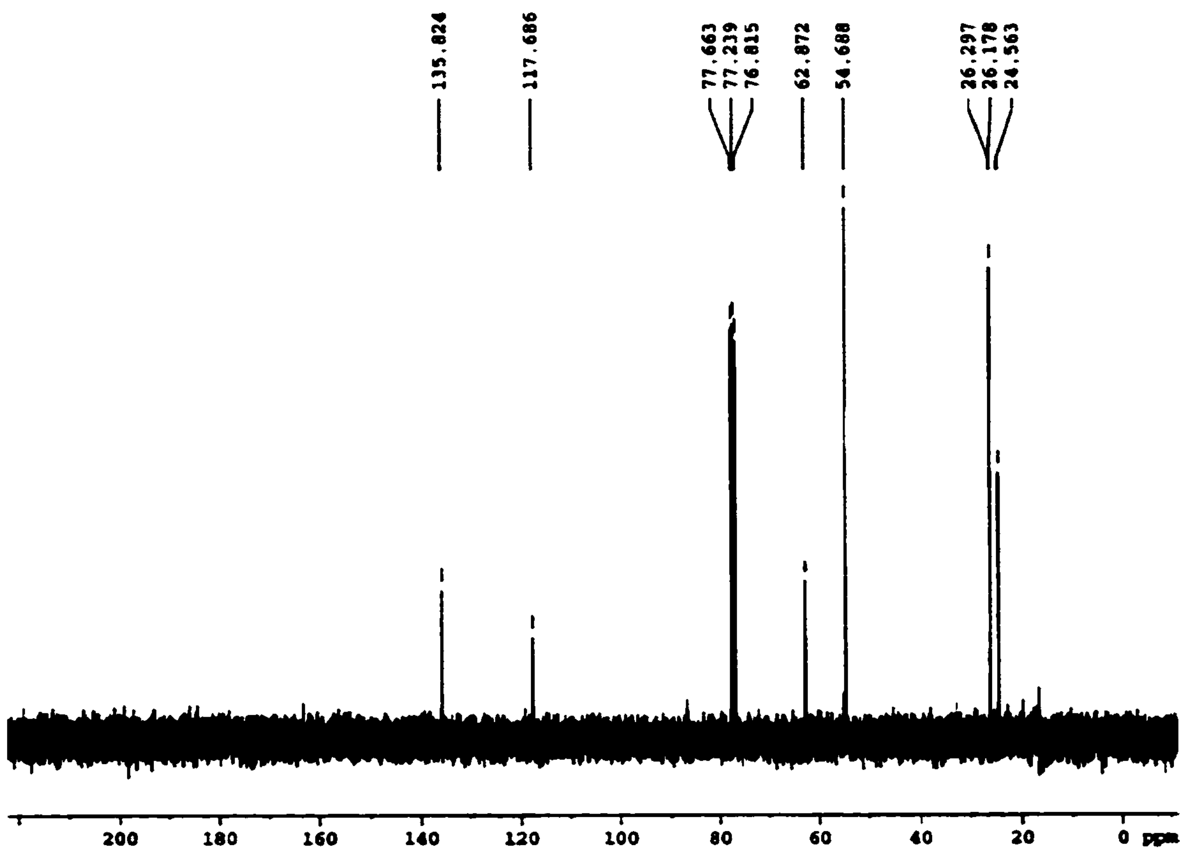
^1H NMR of 2-(*N*-piperidylmethyl)-1,3-butadiene (1).



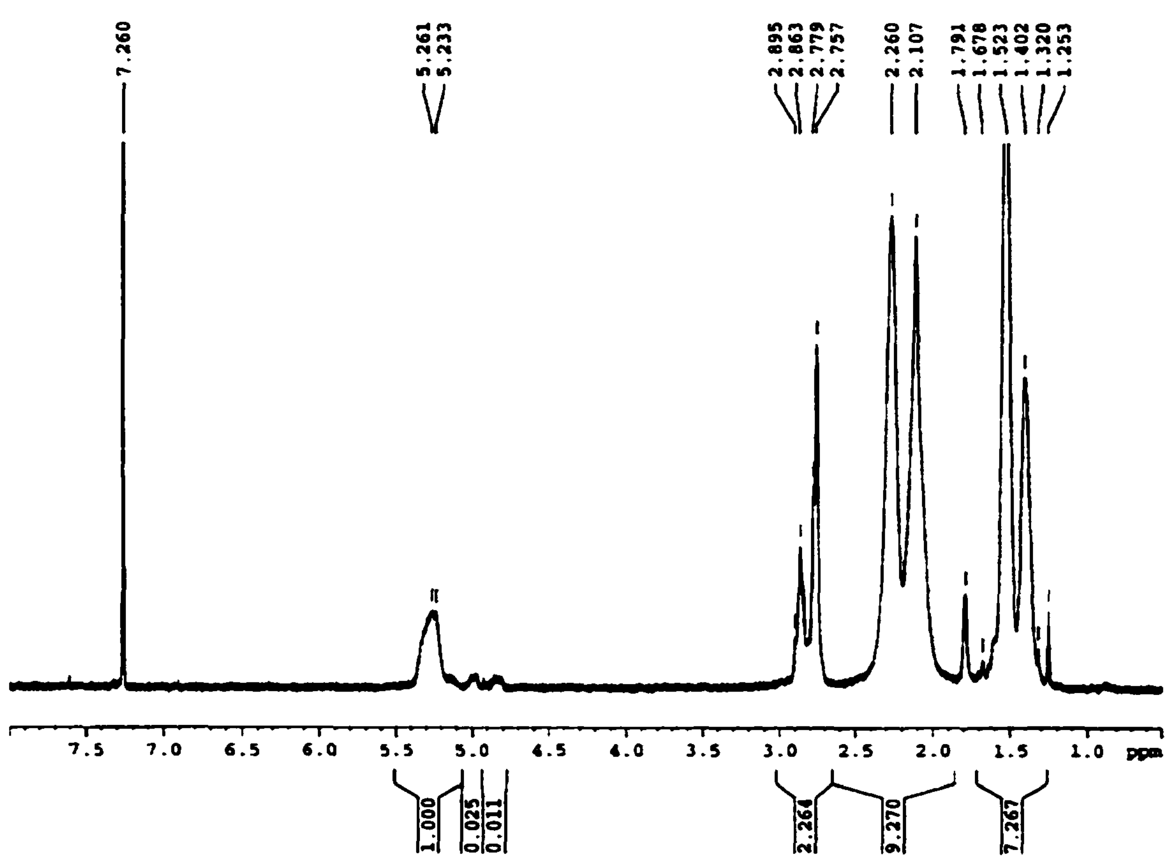
^{13}C NMR of 2-(*N*-piperidylmethyl)-1,3-butadiene (**1**).



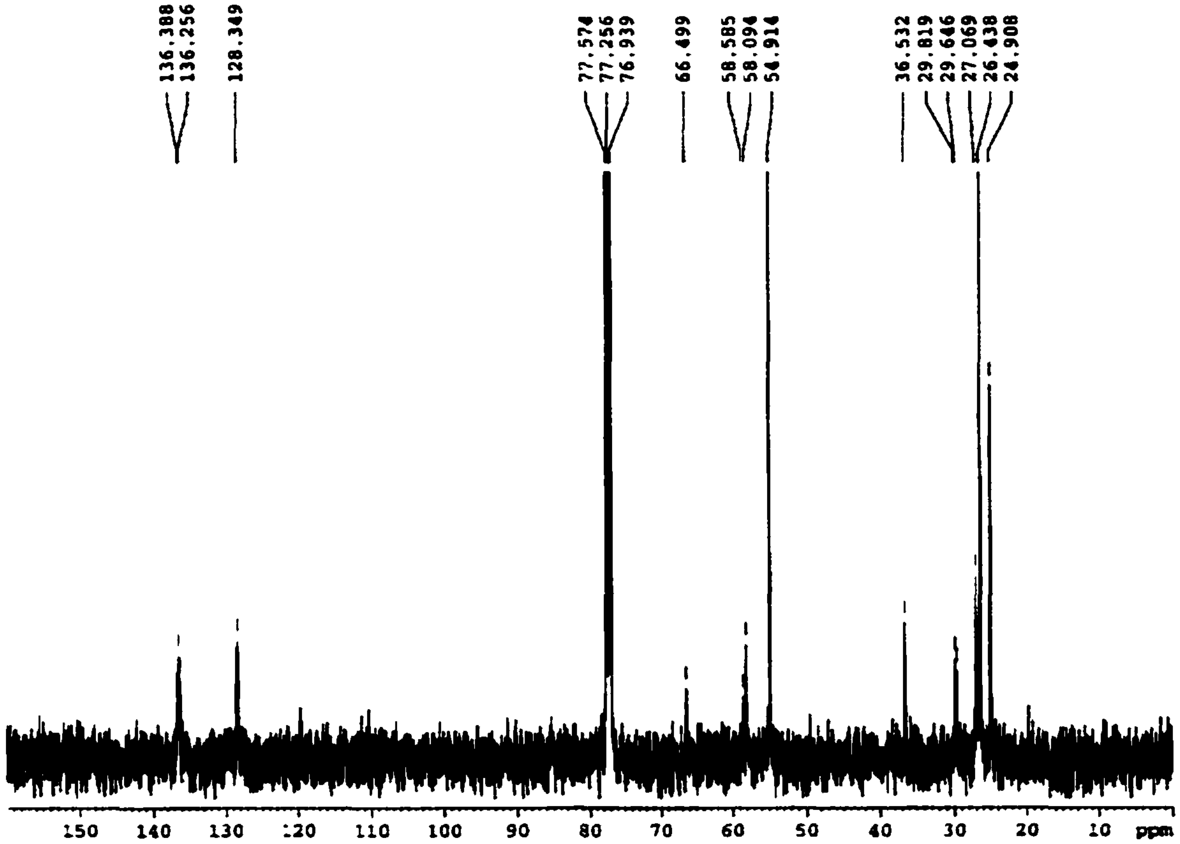
^{1}H NMR of 3-(*N*-piperidyl)-1-propene (**2**).



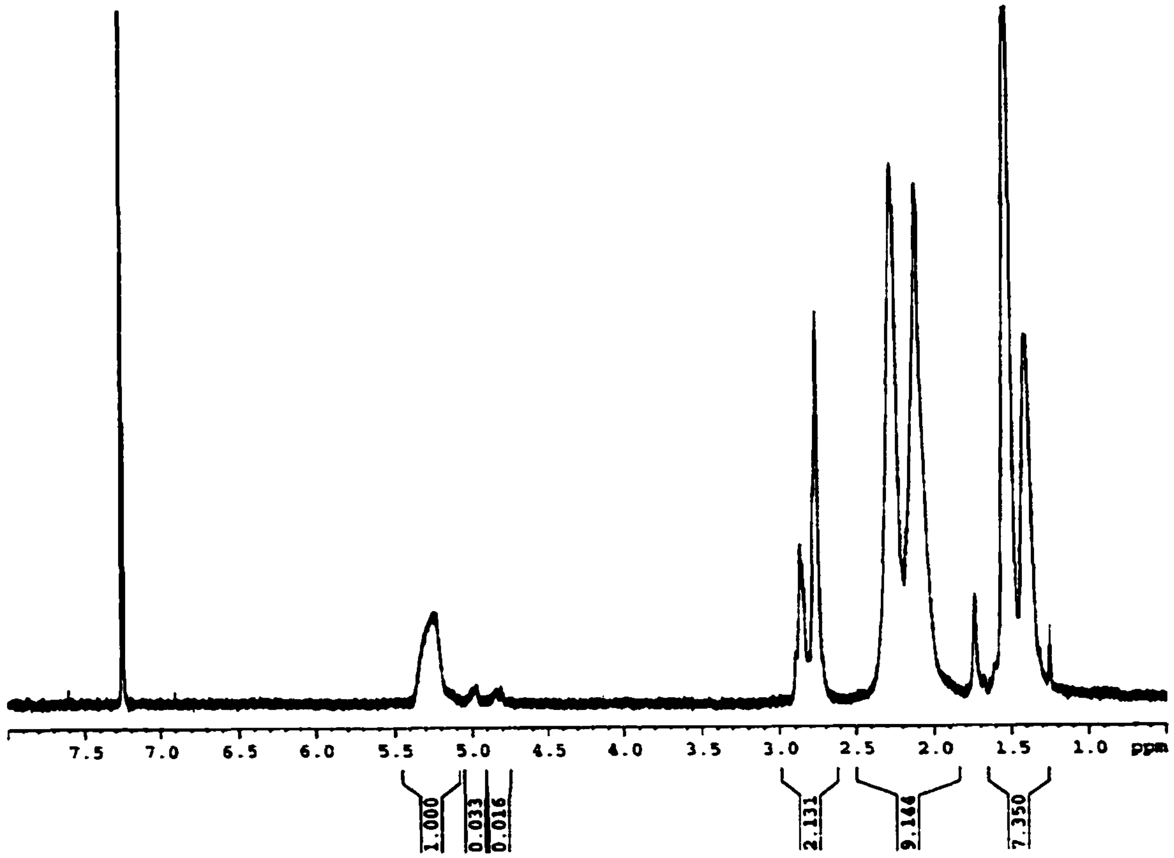
^{13}C NMR of 3-(*N*-piperidyl)-1-propene (**2**).



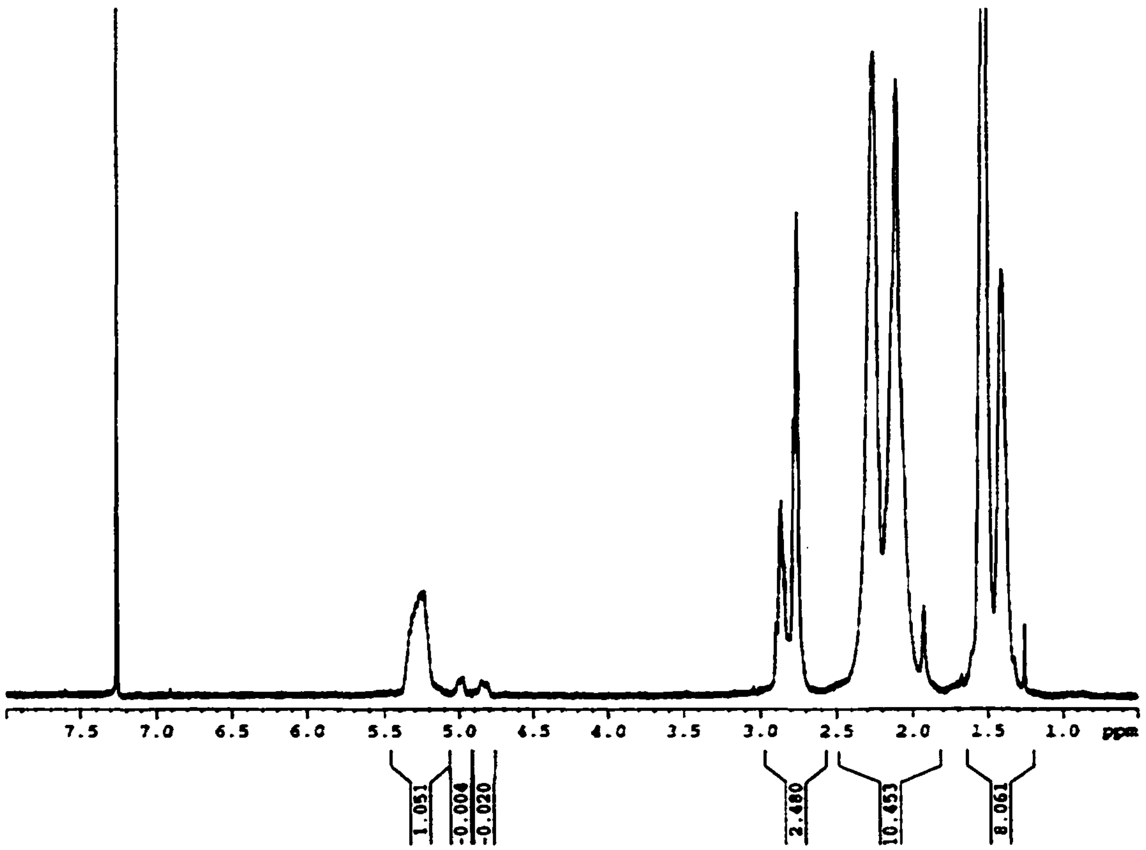
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (3).



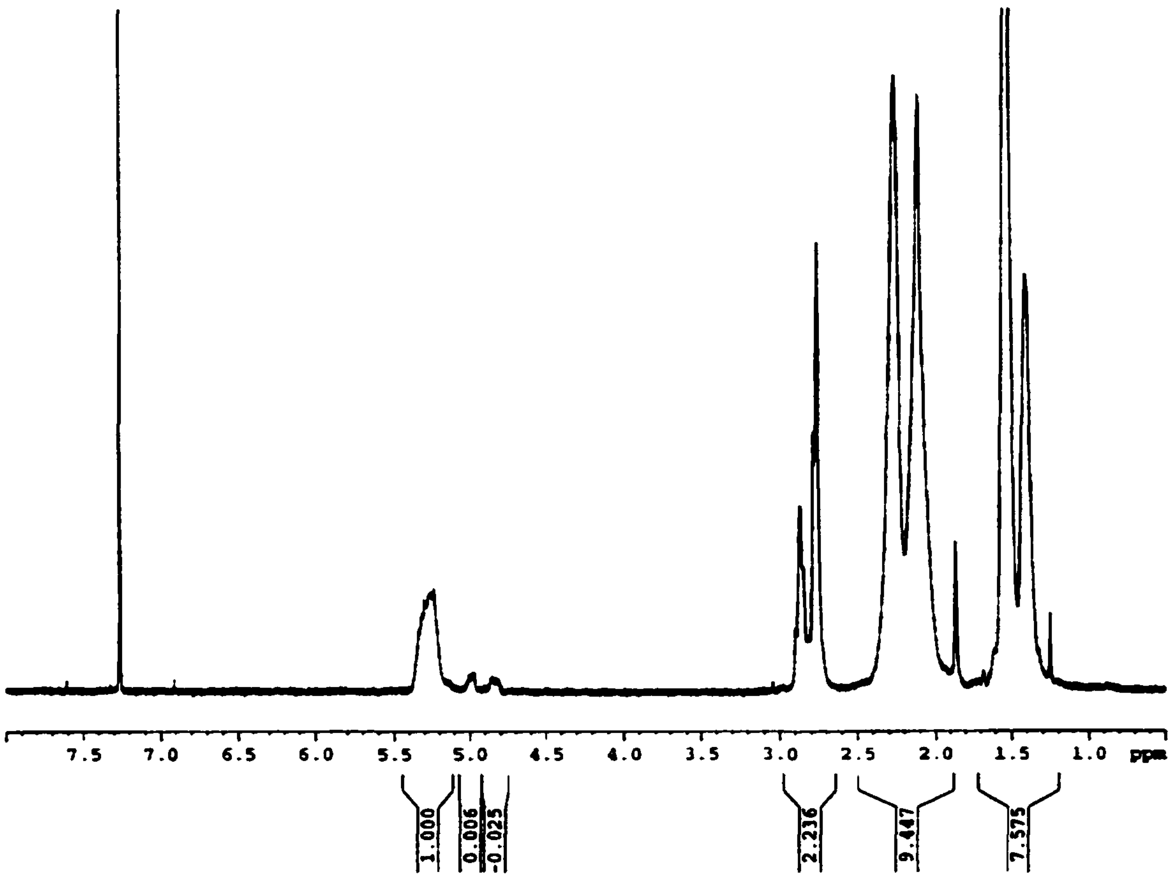
^{13}C NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (3).



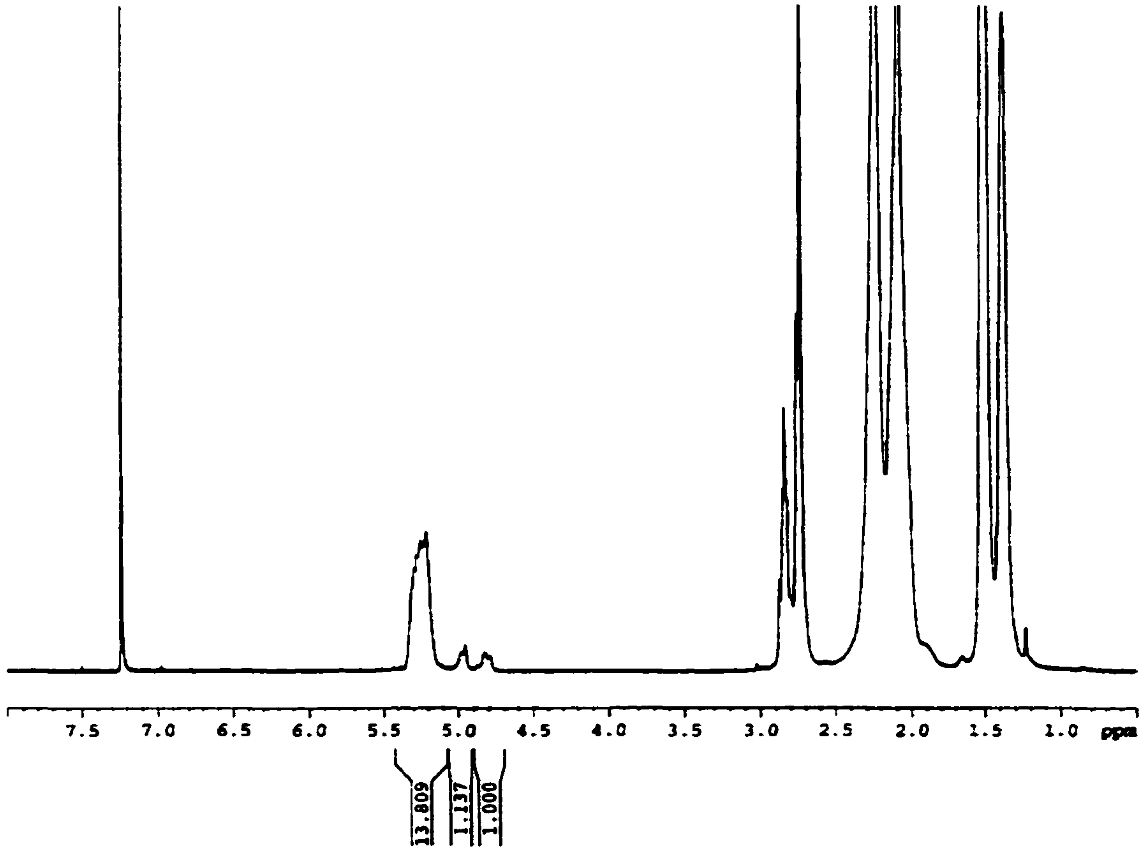
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (4).



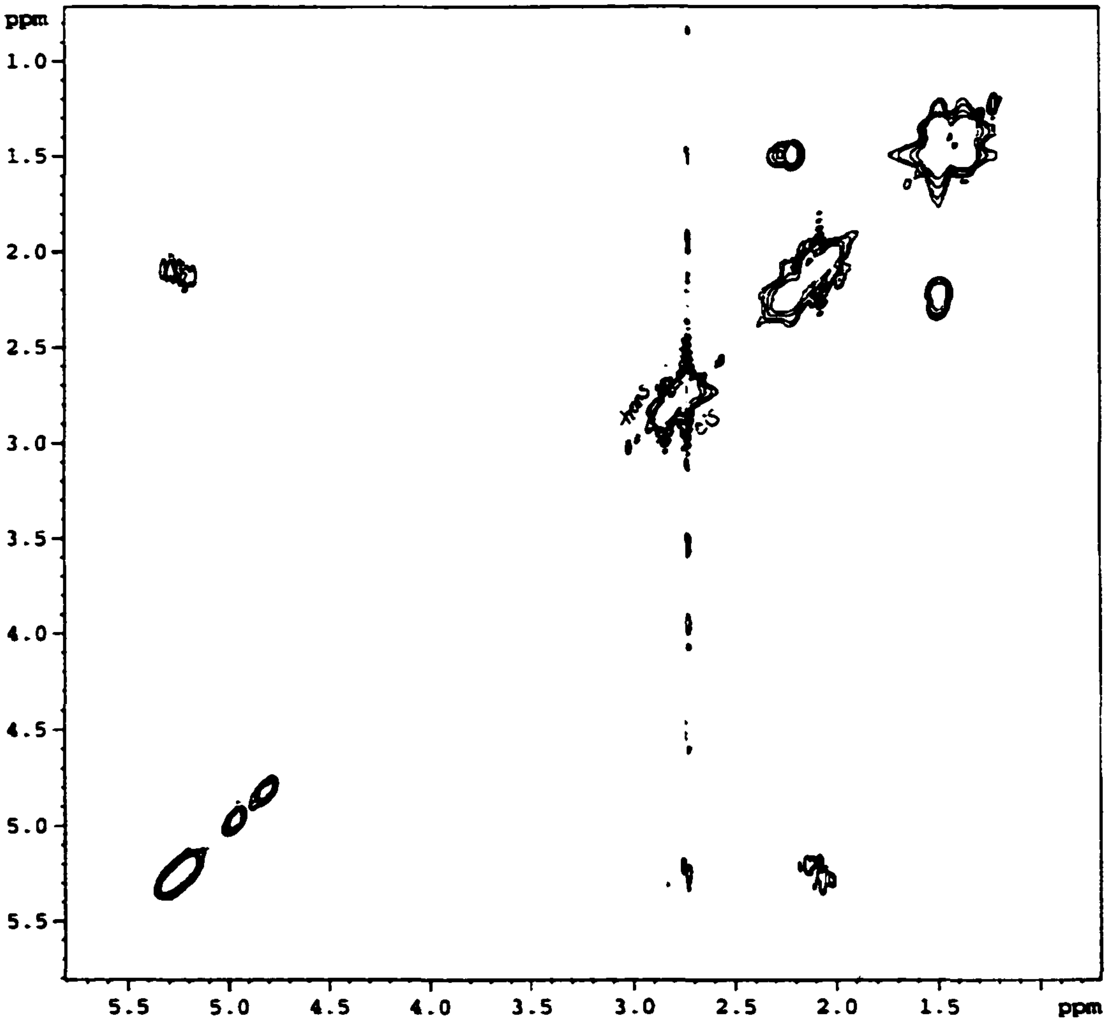
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**5**).



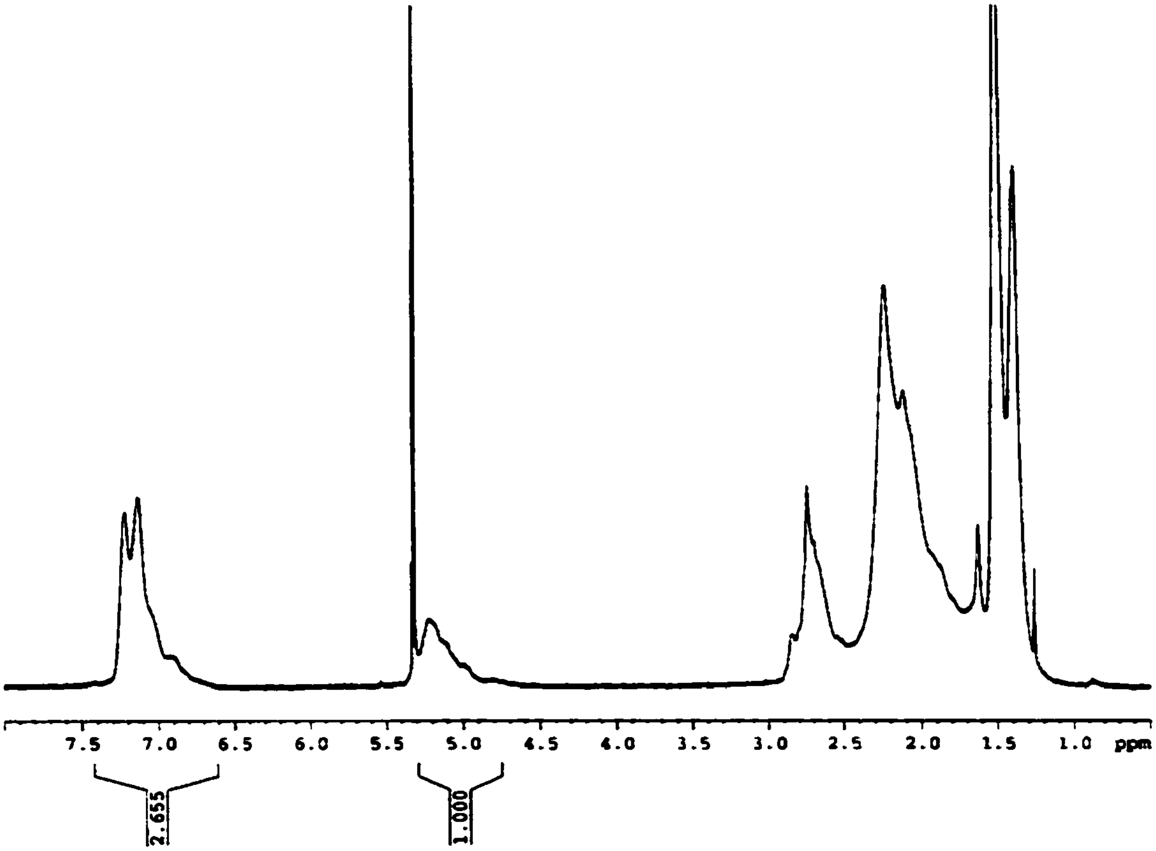
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**6**).



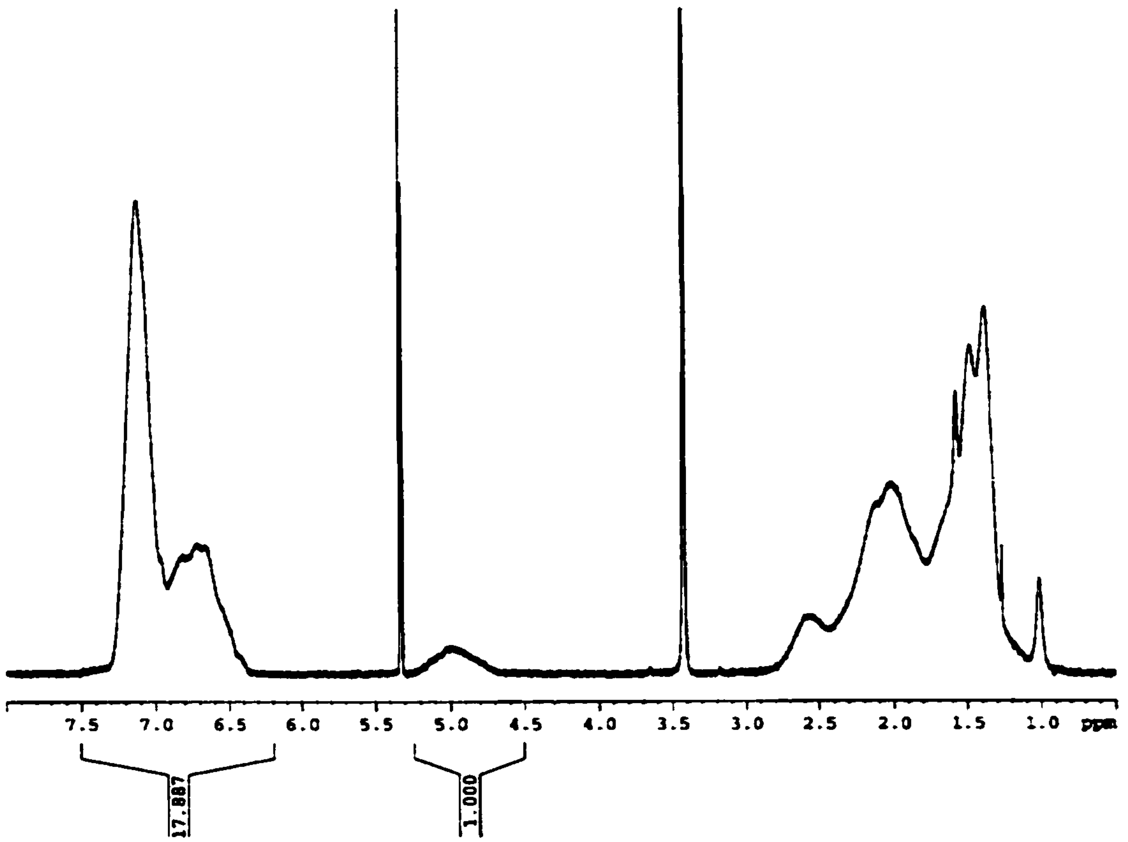
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**11**).



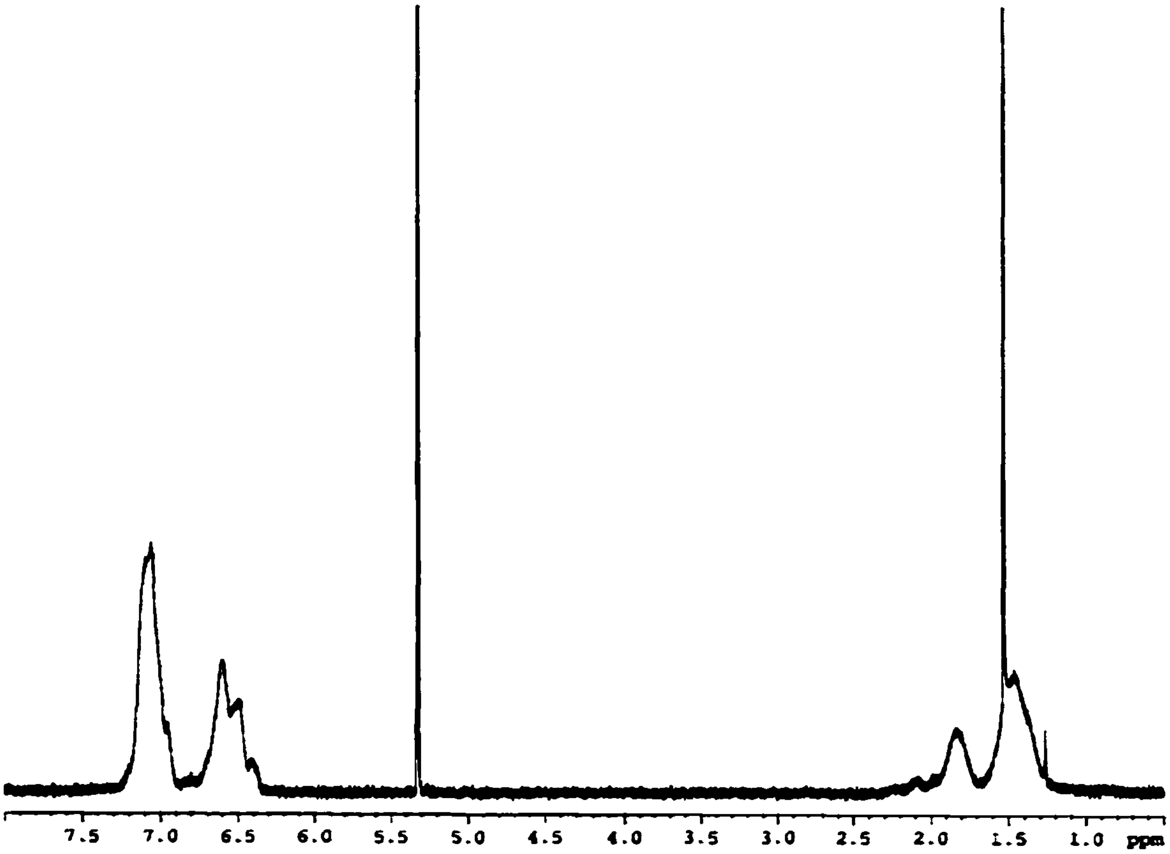
ROESY of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (11).



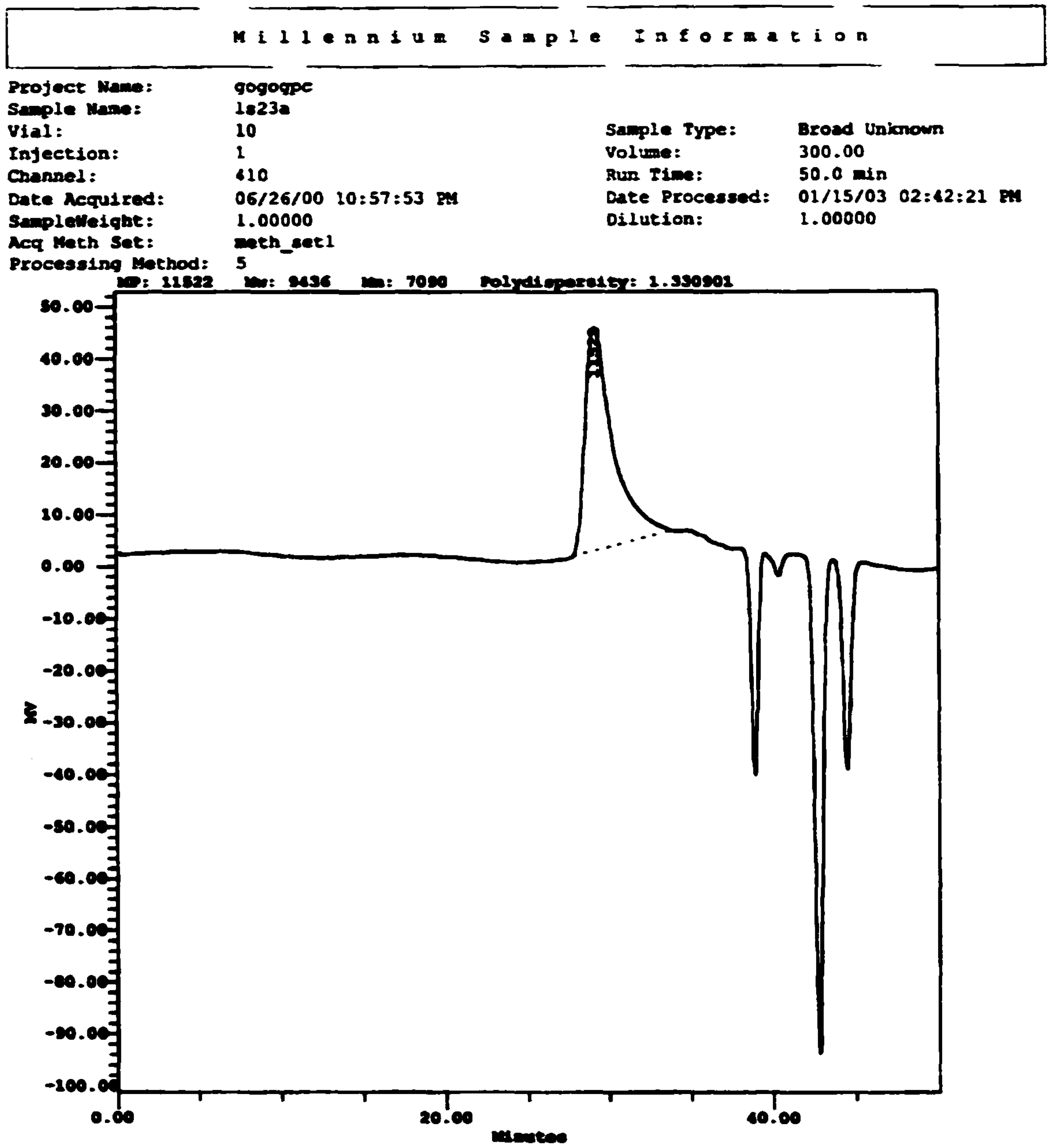
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (**12**).



^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (**13**).



^{1}H NMR of Poly(styrene) (16).

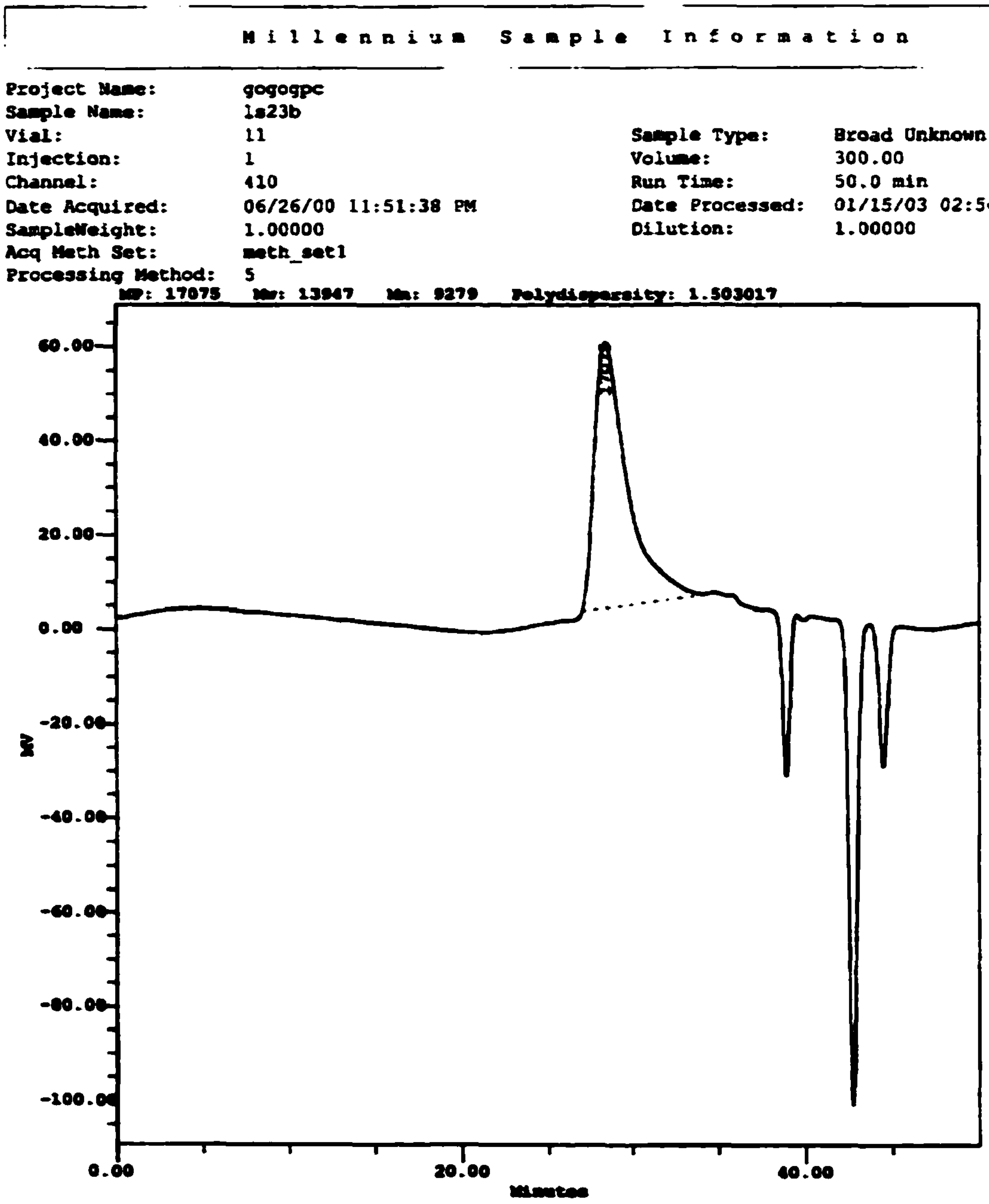


Millennium Sample Information

Project Name:	gogogpc		
Sample Name:	ls23a		
Vial:	10	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	06/26/00 10:57:53 PM	Date Processed:	01/15/03 02:42:21 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	5		

MP: 11522 Mw: 9436 Mn: 7090 Polydispersity: 1.330901

GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (3).



Millennium Sample Information

Project Name: gogogpc
Sample Name: ls23b
Vial: 11
Injection: 1
Channel: 410
Date Acquired: 06/26/00 11:51:38 PM
SampleWeight: 1.00000
Acq Meth Set: meth_set1
Processing Method: 5

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 01/15/03 02:54:23 PM
Dilution: 1.00000

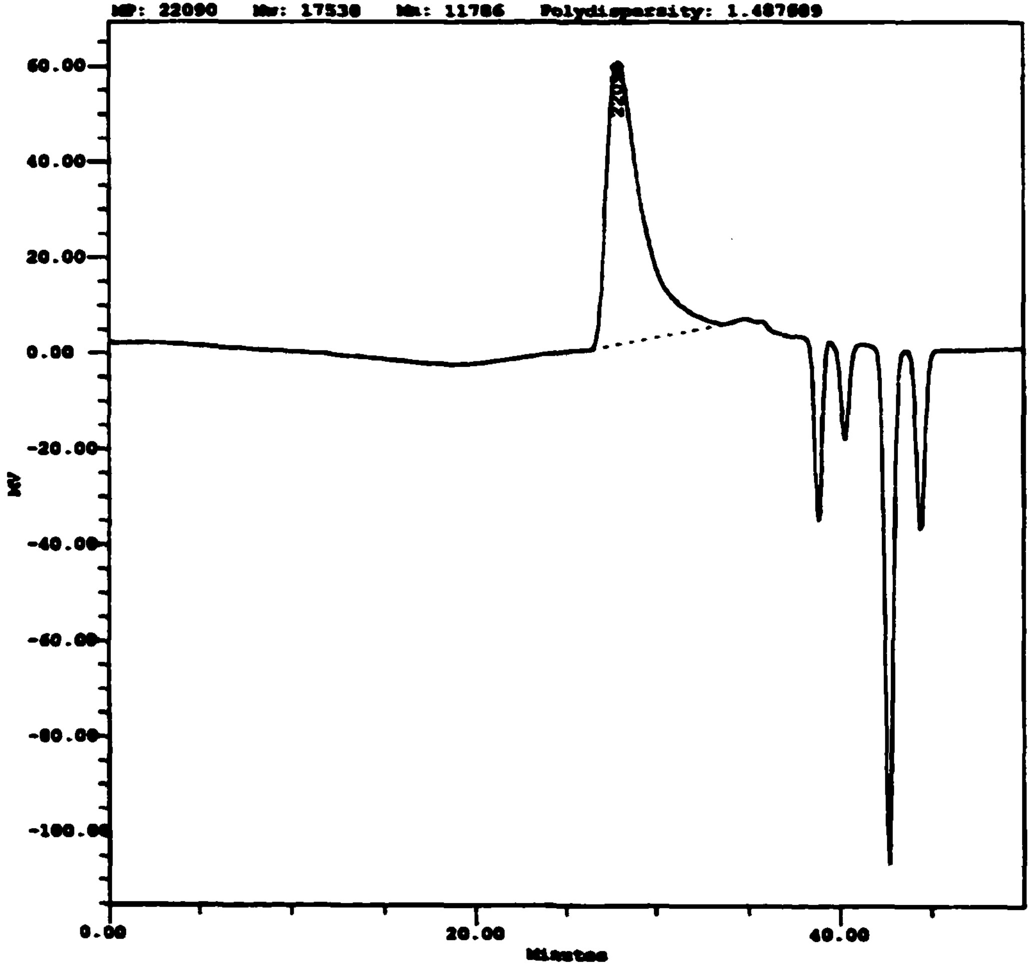
MP: 17075 Mw: 13947 Mn: 9279 Polydispersity: 1.503017

GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (4).

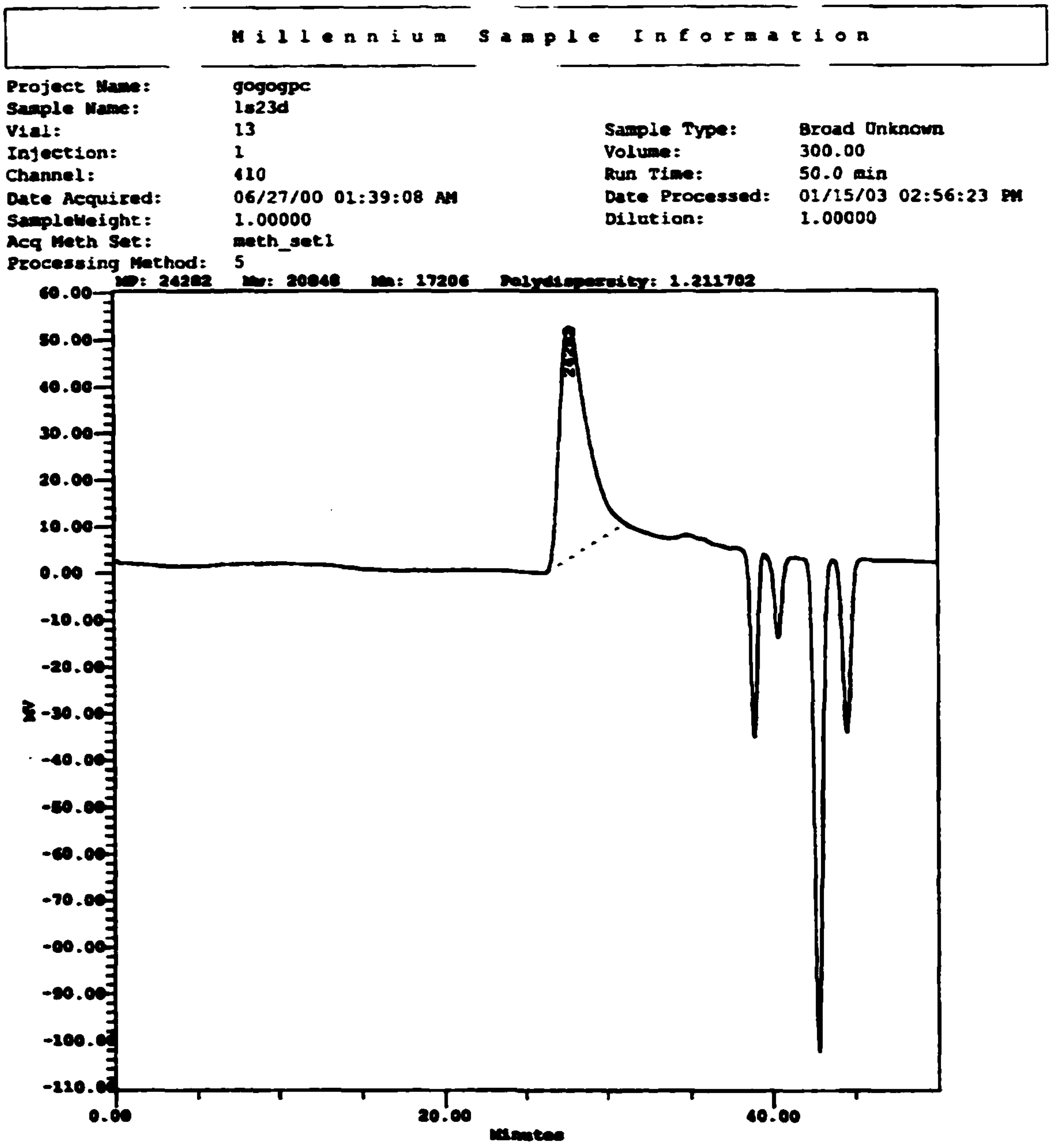
Millennium Sample Information

Project Name:	goqoqpc		
Sample Name:	ls23c		
Vial:	12	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	06/27/00 12:45:23 AM	Date Processed:	01/15/03 02:55:19 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	5		

MP: 22090 Mw: 17530 Mn: 11786 Polydispersity: 1.487609



GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**5**).



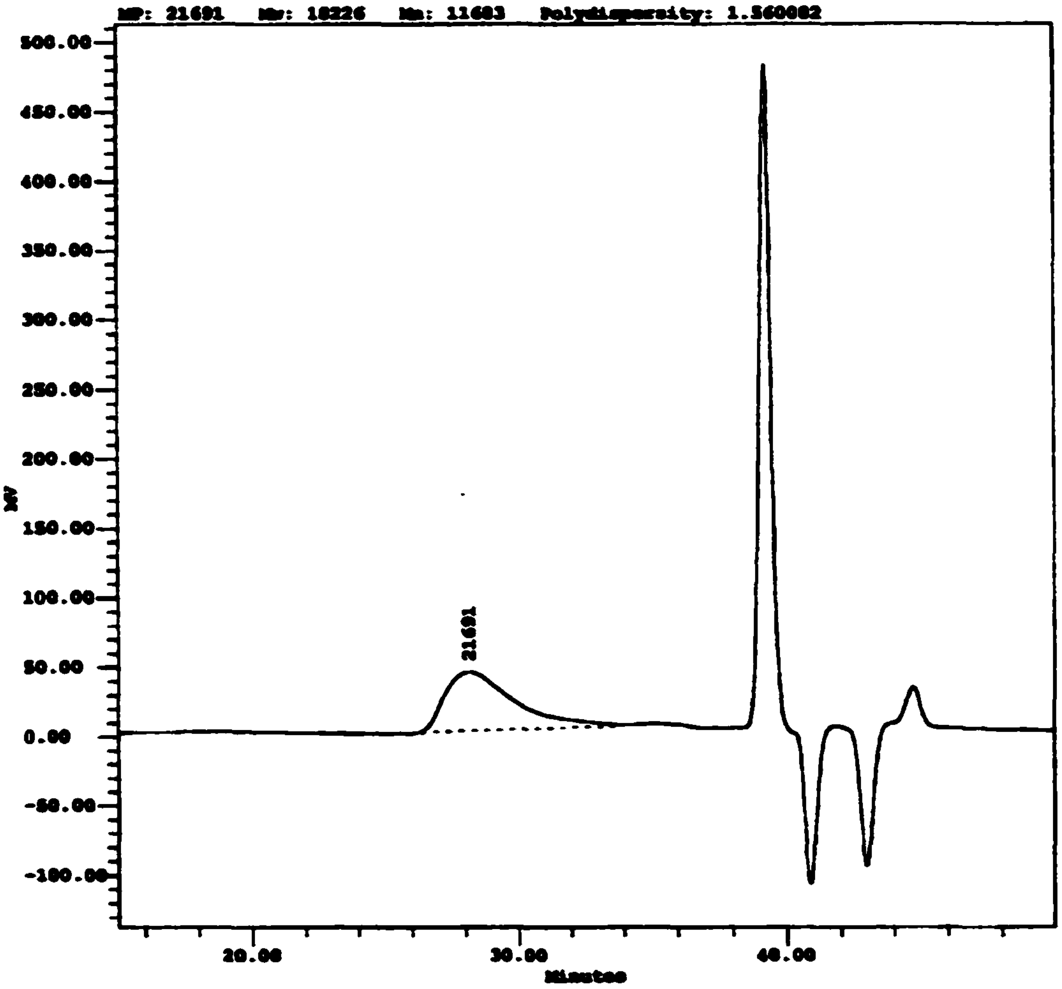
```
                    M i l l e n n i u m   S a m p l e   I n f o r m a t i o n

Project Name:         gogogpc
Sample Name:          ls23d
Vial:                 13                                Sample Type:        Broad Unknown
Injection:            1                                 Volume:             300.00
Channel:              410                               Run Time:           50.0 min
Date Acquired:        06/27/00 01:39:08 AM              Date Processed:     01/15/03 02:56:23 PM
SampleWeight:         1.00000                           Dilution:           1.00000
Acq Meth Set:         meth_set1
Processing Method:    5
      MP: 24282   Mw: 20848   Mn: 17206   Polydispersity: 1.211702
```

GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (6).

Millennium Sample Information

Project Name:	gogogpc		
Sample Name:	1a229g		
Vial:	7	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	08/23/00 04:37:29 AM	Date Processed:	08/28/00 11:12:36 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	tarkenton		



GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (11).

```
                    M i l l e n n i u m   S a m p l e   I n f o r m a t i o n

Project Name:        gogogpc
Sample Name:         ls227a
Vial:                1                            Sample Type:      Broad Unknown
Injection:           2                            Volume:           300.00
Channel:             410                          Run Time:         50.0 min
Date Acquired:       08/22/00 11:15:00 PM         Date Processed:   08/28/00 11:09:54 AM
SampleWeight:        1.00000                      Dilution:         1.00000
Acq Meth Set:        meth_set1
Processing Method:   tarkenton
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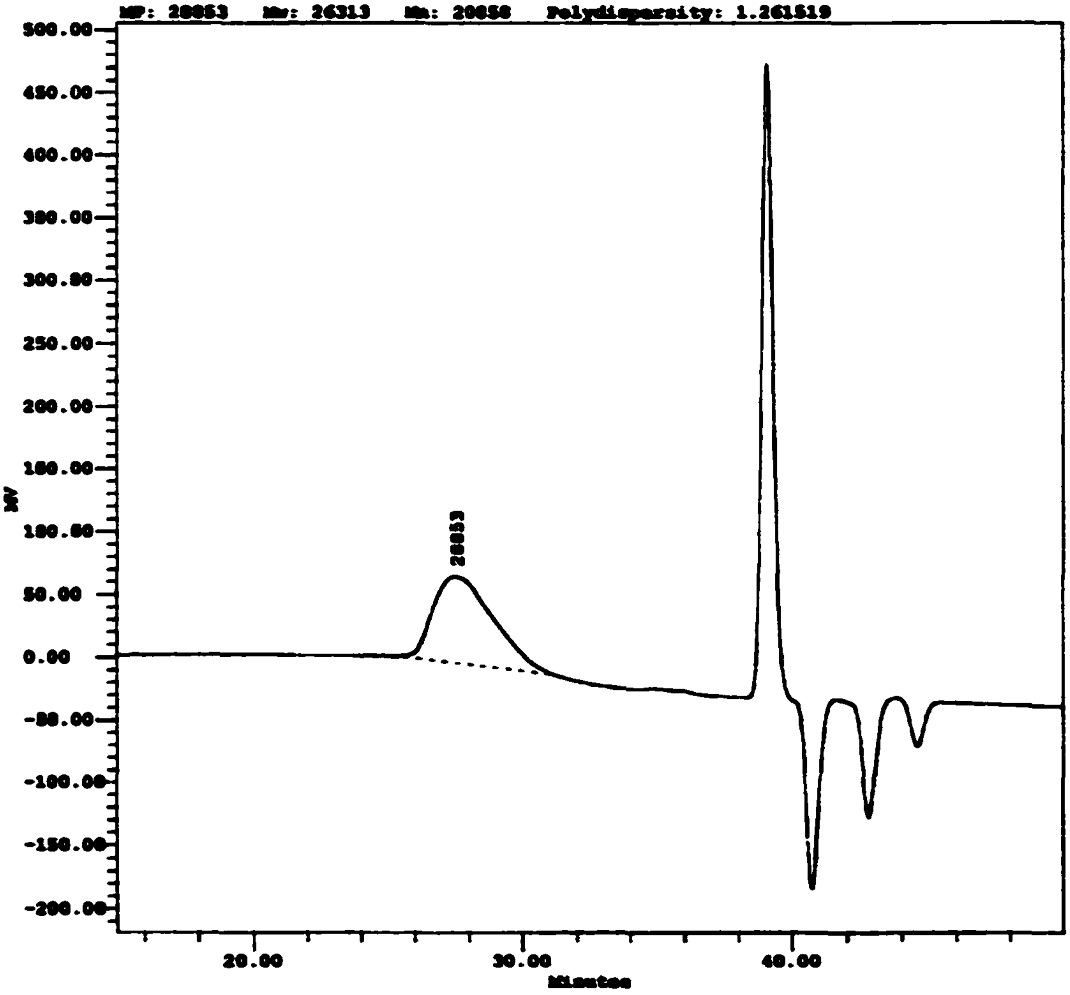
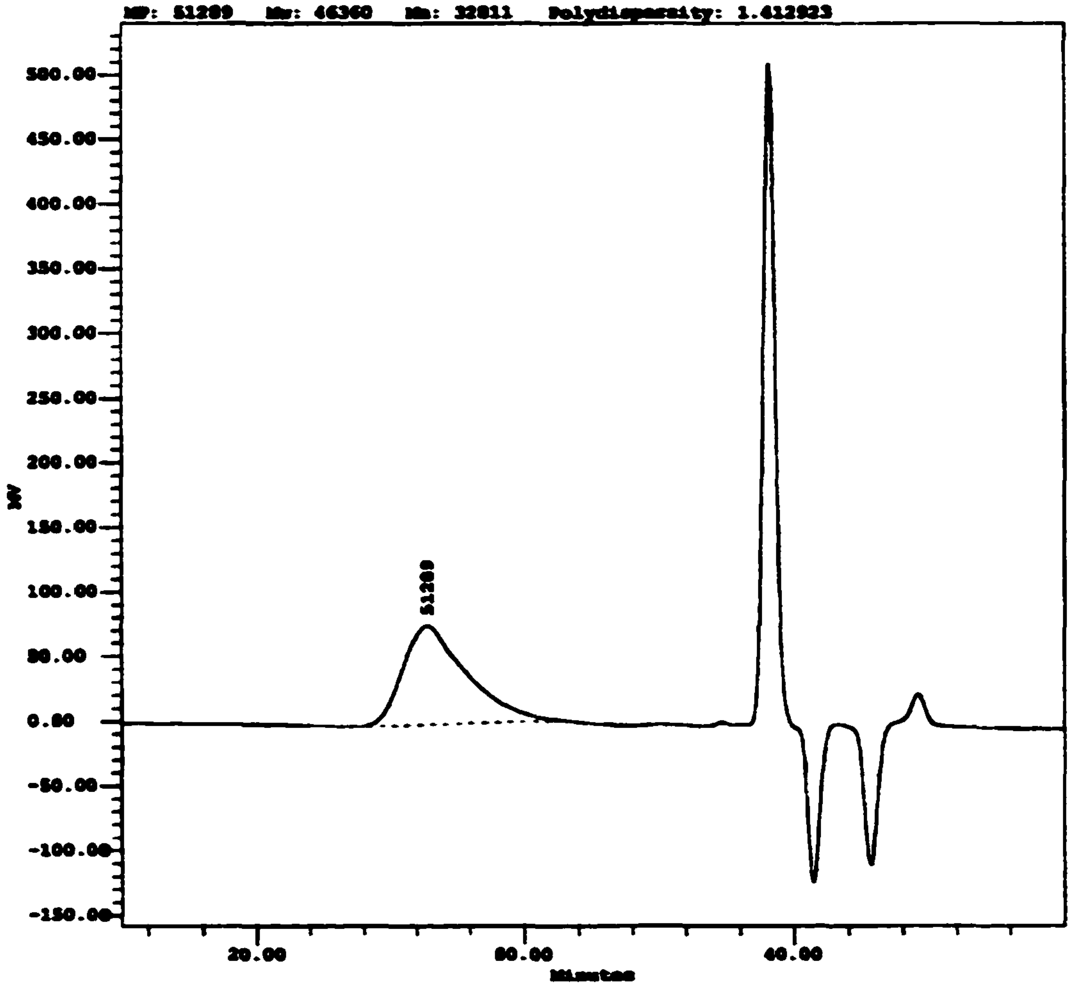


GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (12).

Millennium Sample Information

Project Name:	goqogpc		
Sample Name:	ls227b		
Vial:	2	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	08/23/00 12:08:49 AM	Date Processed:	08/28/00 11:10:19 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	tarkenton		

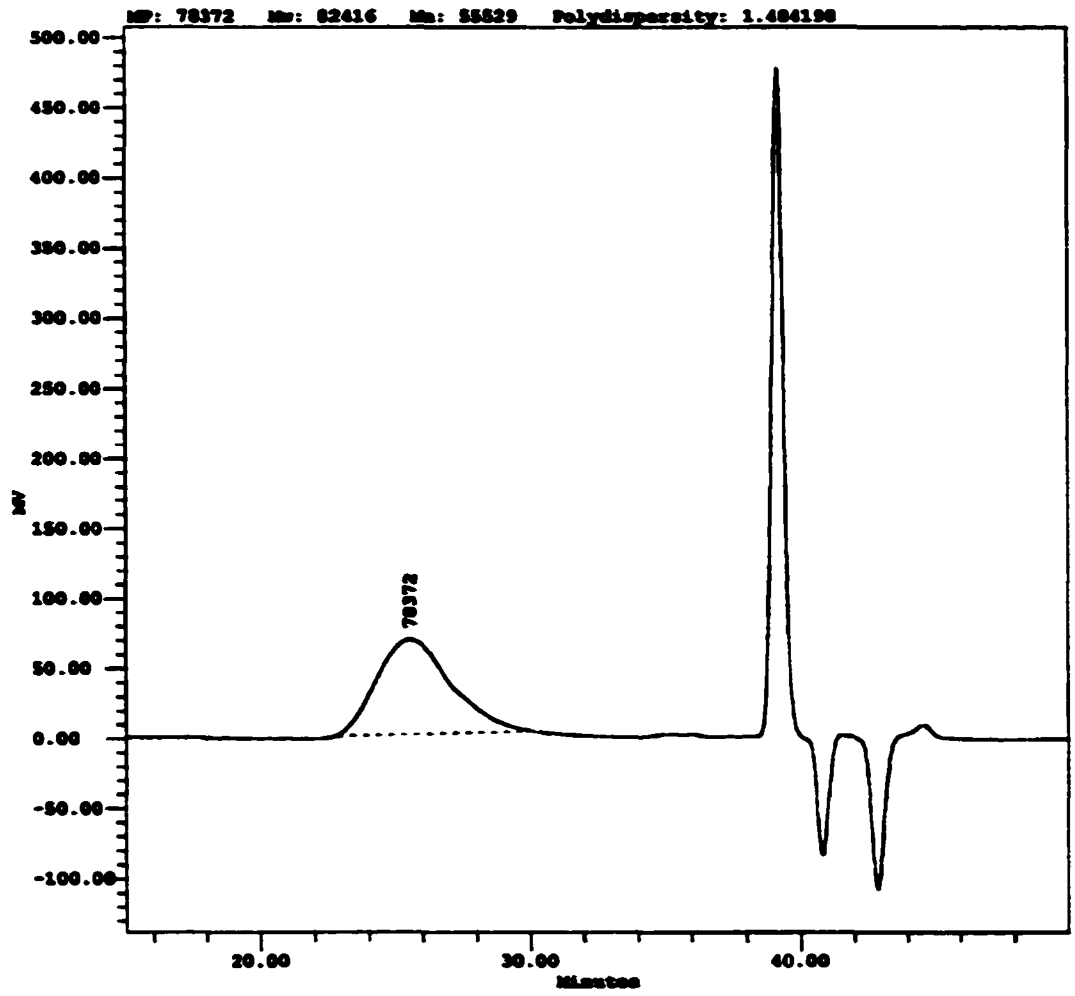
MP: 51289 Mw: 46360 Mn: 32811 Polydispersity: 1.412923



GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (13).

```
                    Millennium Sample Information

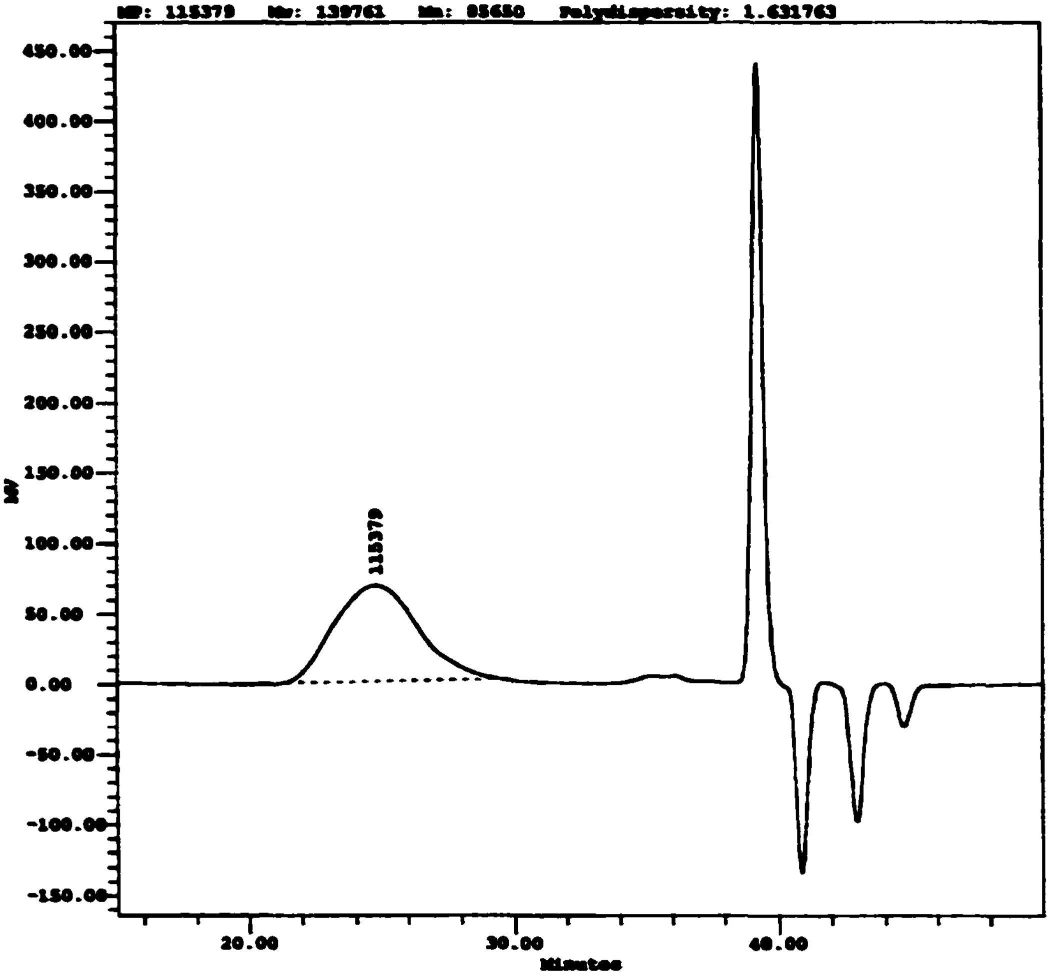
Project Name:        gogogpc
Sample Name:         ls227c
Vial:                3                         Sample Type:       Broad Unknown
Injection:           1                         Volume:            300.00
Channel:             410                       Run Time:          50.0 min
Date Acquired:       08/23/00 01:02:34 AM      Date Processed:    08/28/00 11:10:47 AM
SampleWeight:        1.00000                   Dilution:          1.00000
Acq Meth Set:        meth_set1
Processing Method:   tarkenton
```



GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (14).

```
                    Millennium Sample Information

Project Name:         gogogpc
Sample Name:          ls229d
Vial:                 4                         Sample Type:       Broad Unknown
Injection:            1                         Volume:            300.00
Channel:              410                       Run Time:          50.0 min
Date Acquired:        08/23/00 01:56:20 AM      Date Processed:    08/28/00 11:11:11 AM
SampleWeight:         1.00000                   Dilution:          1.00000
Acq Meth Set:         meth_set1
Processing Method:    tarkenton
```

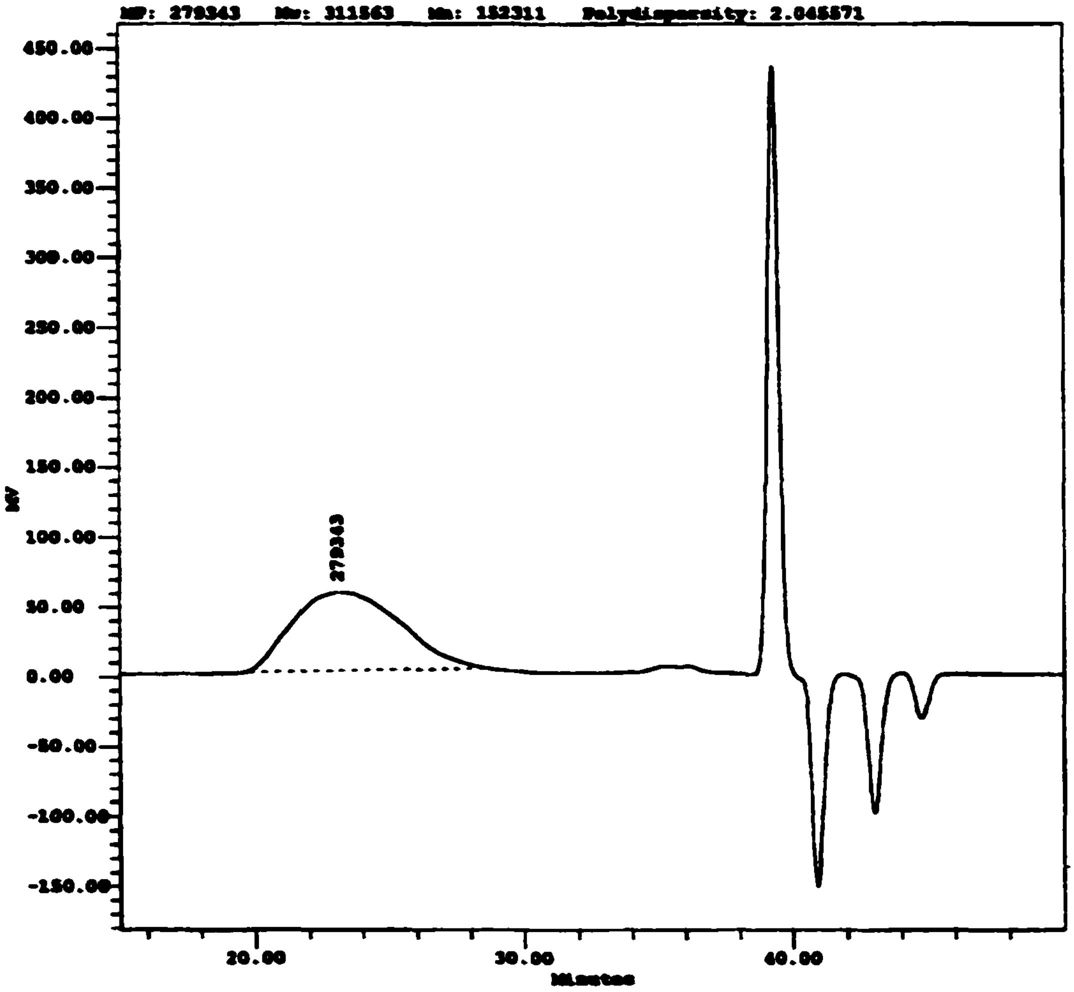


MP: 115379   Mw: 139761   Mn: 85650   Polydispersity: 1.631763

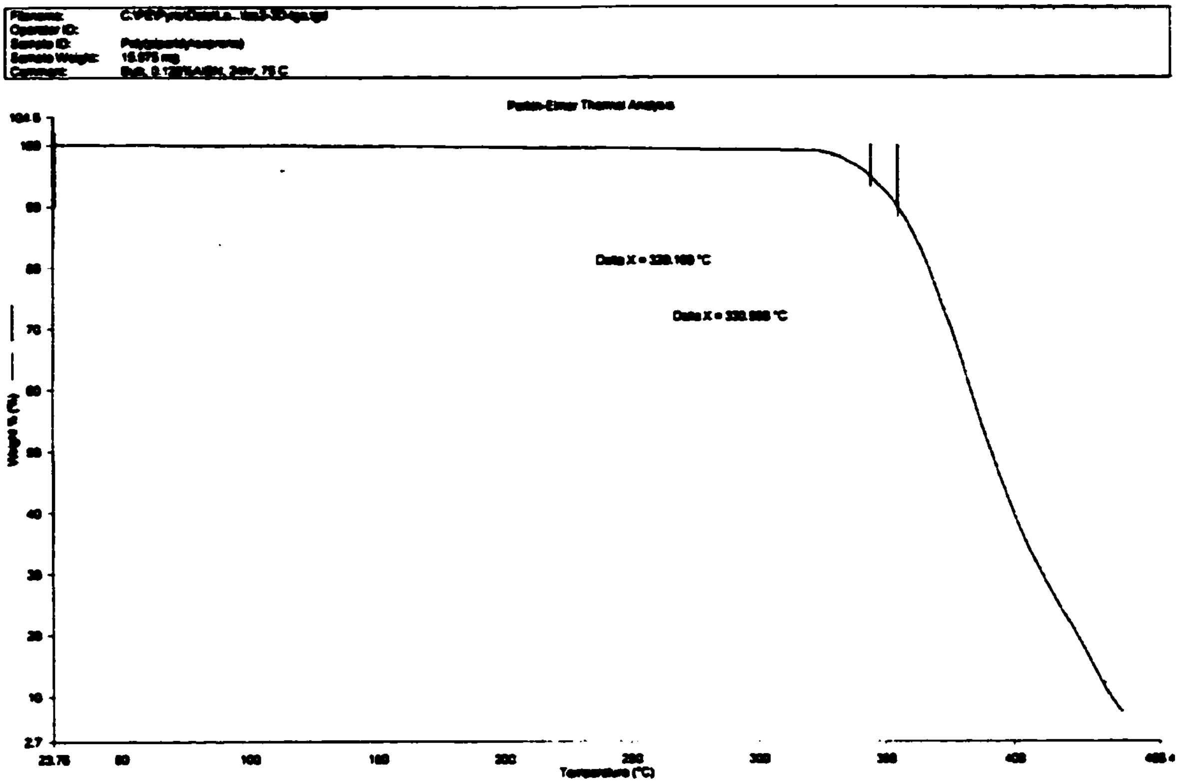
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (15).

Millennium Sample Information

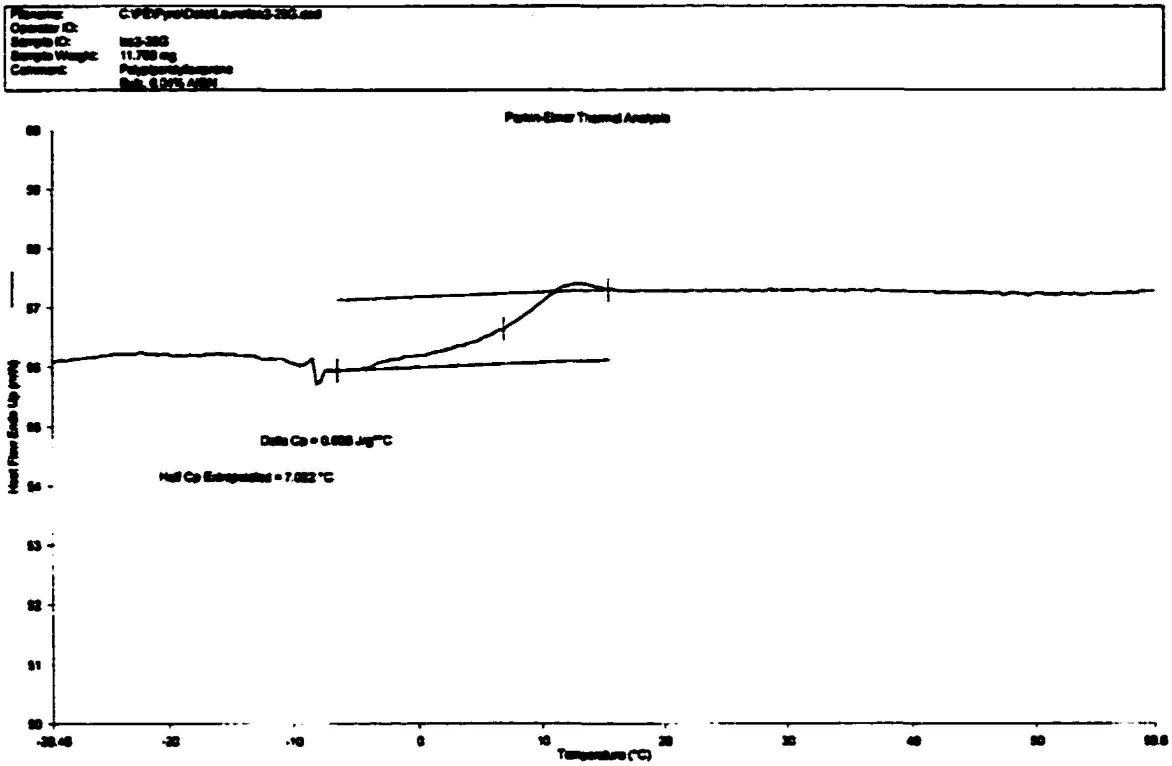
Project Name:	gogogpc		
Sample Name:	ls229f		
Vial:	6	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	410	Run Time:	50.0 min
Date Acquired:	08/23/00 03:43:46 AM	Date Processed:	08/28/00 11:12:06 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	meth_set1		
Processing Method:	tarkenton		



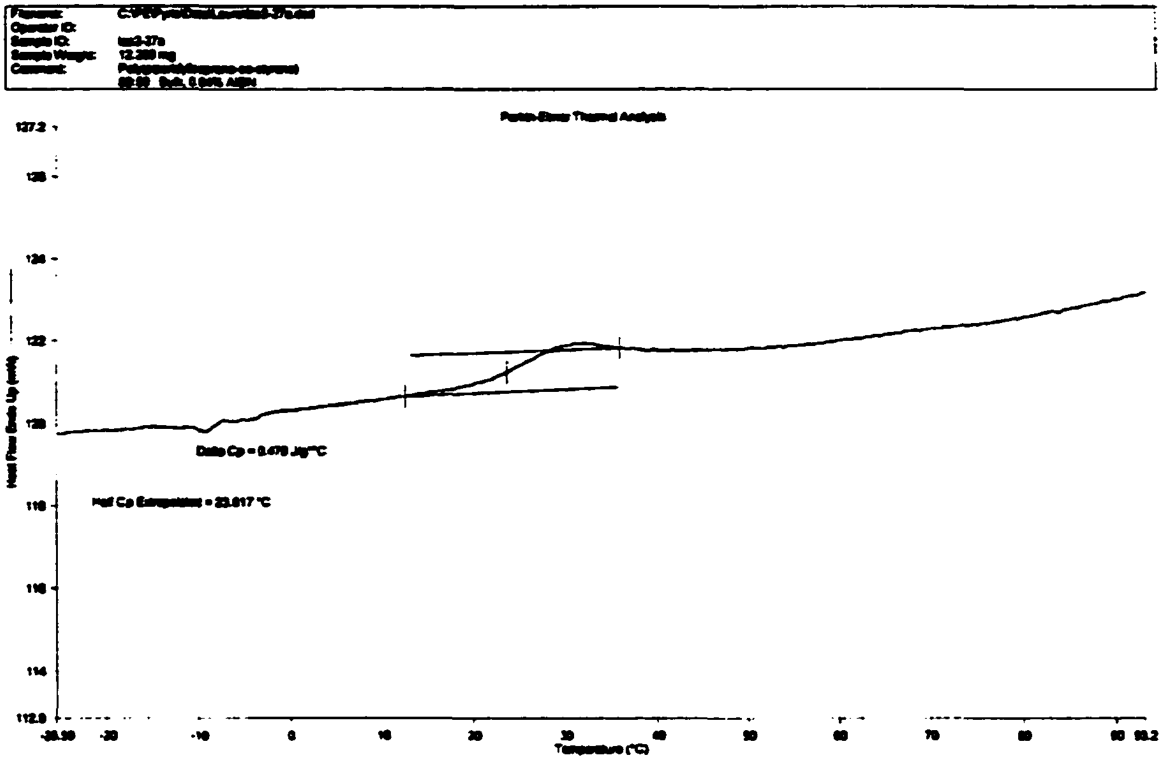
GPC of Poly(styrene) (16).



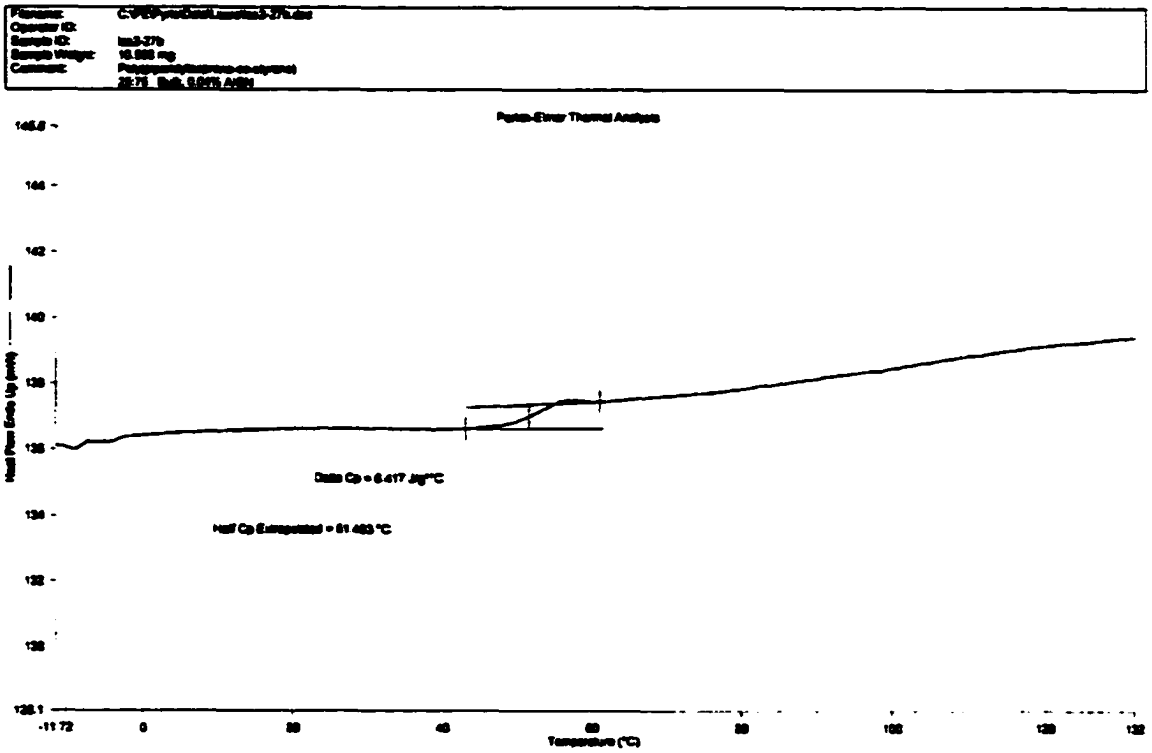
TGA in nitrogen of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (6).



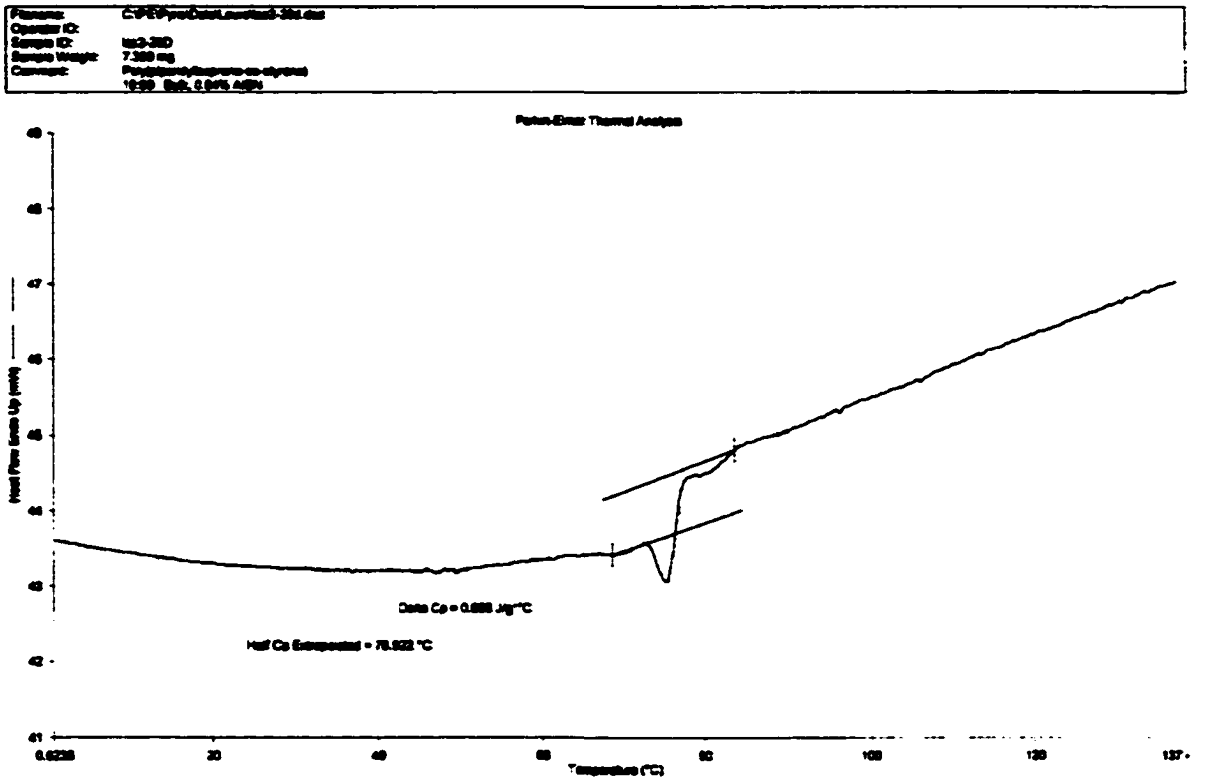
DSC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (11).



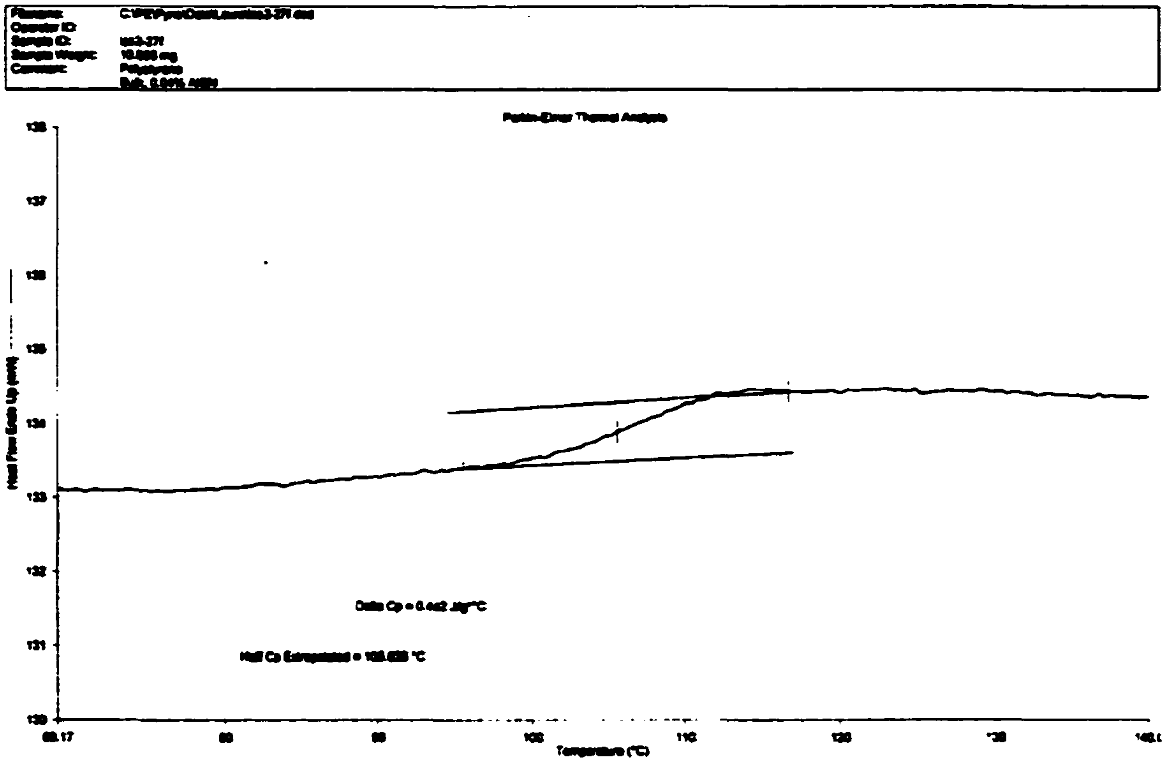
DSC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (12).



DSC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (13).

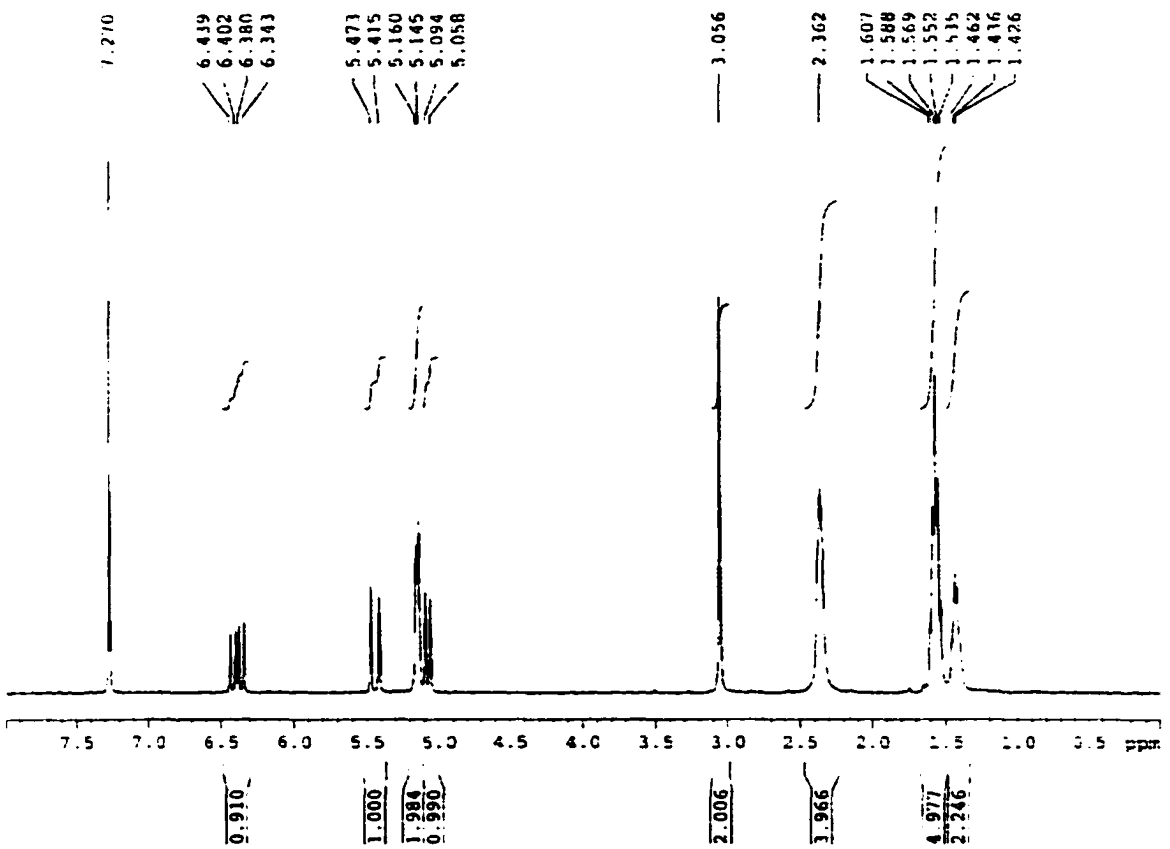


DSC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (15).

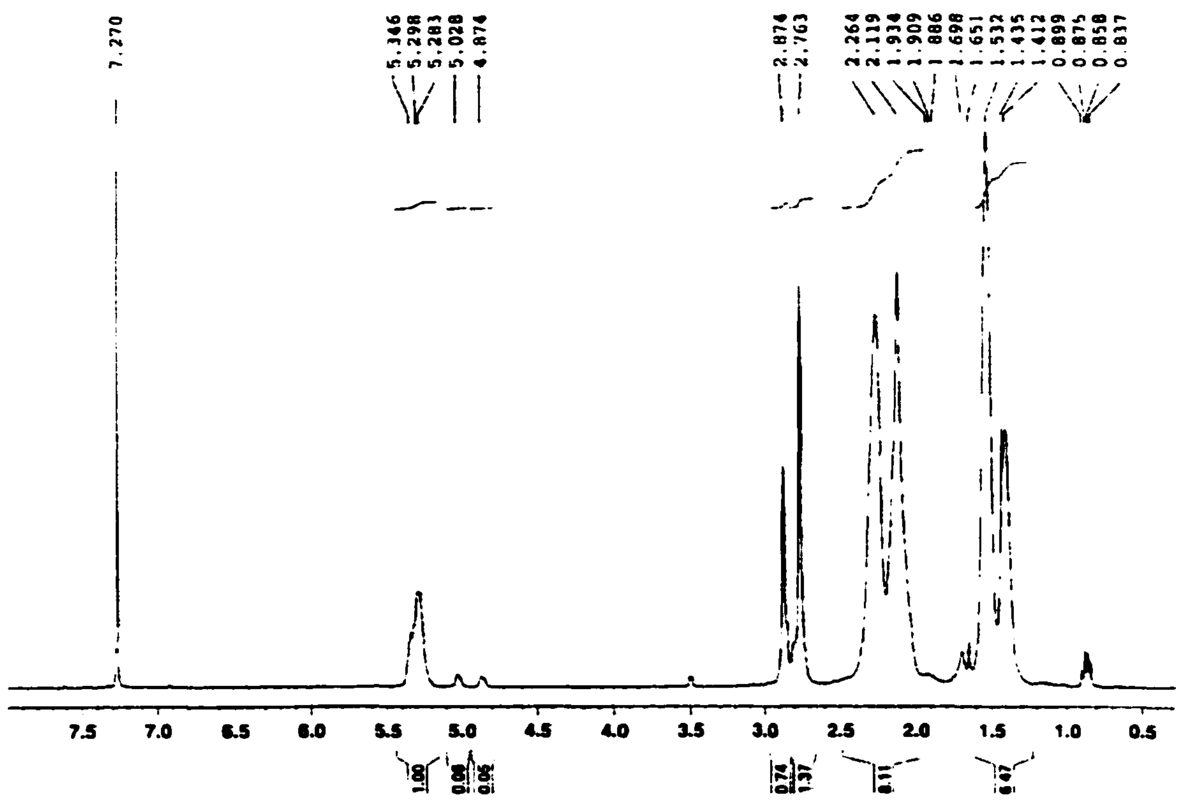


DSC of Poly(styrene) (16).

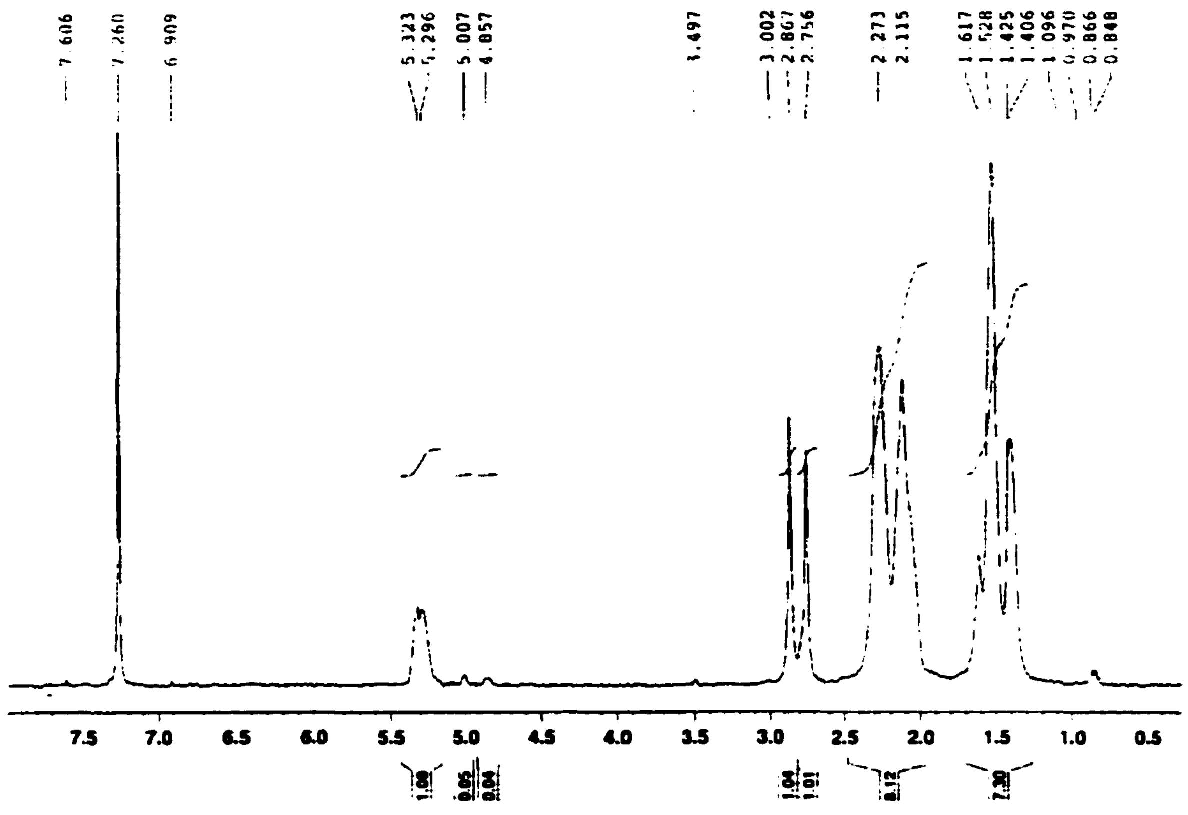
APPENDIX B. SUPPEMENTAL DATA FOR CHAPTER 3



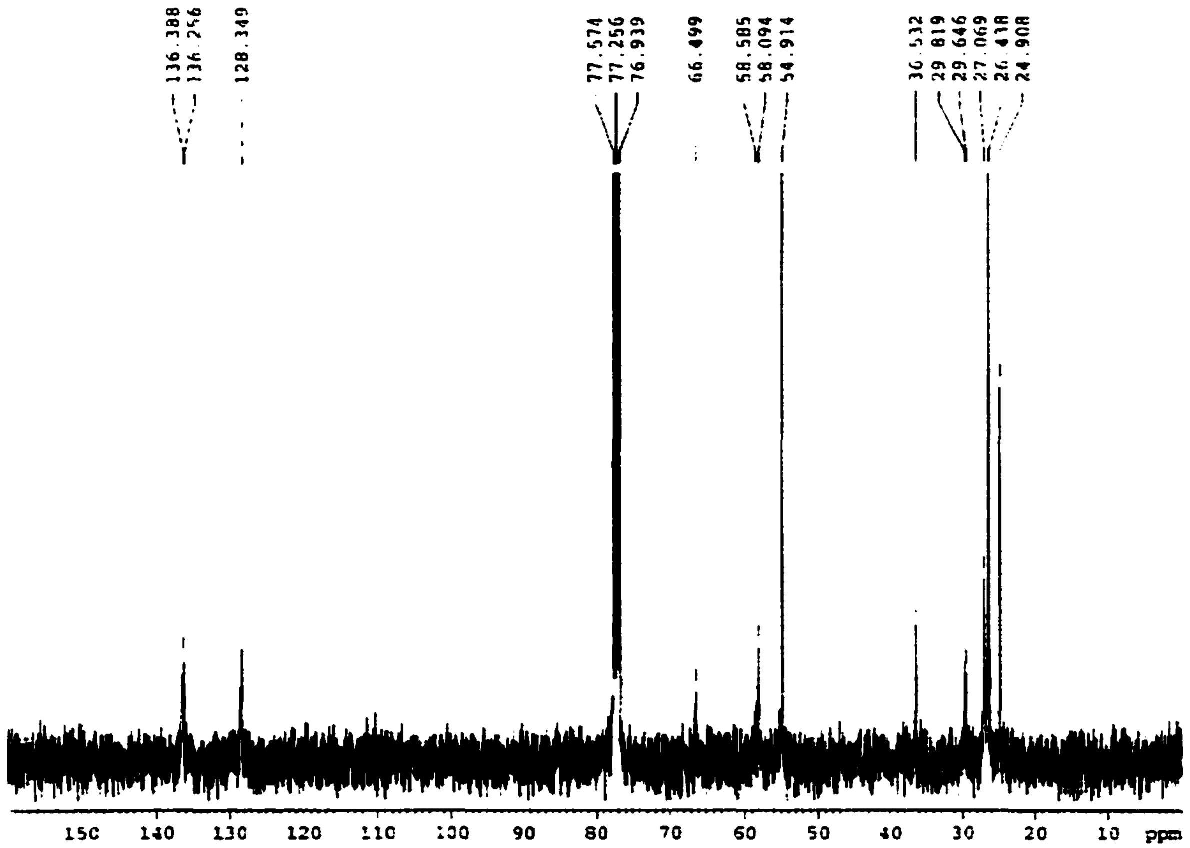
^{1}H NMR of 2-(*N*-piperidylmethyl)-1,3-butadiene (PMB).



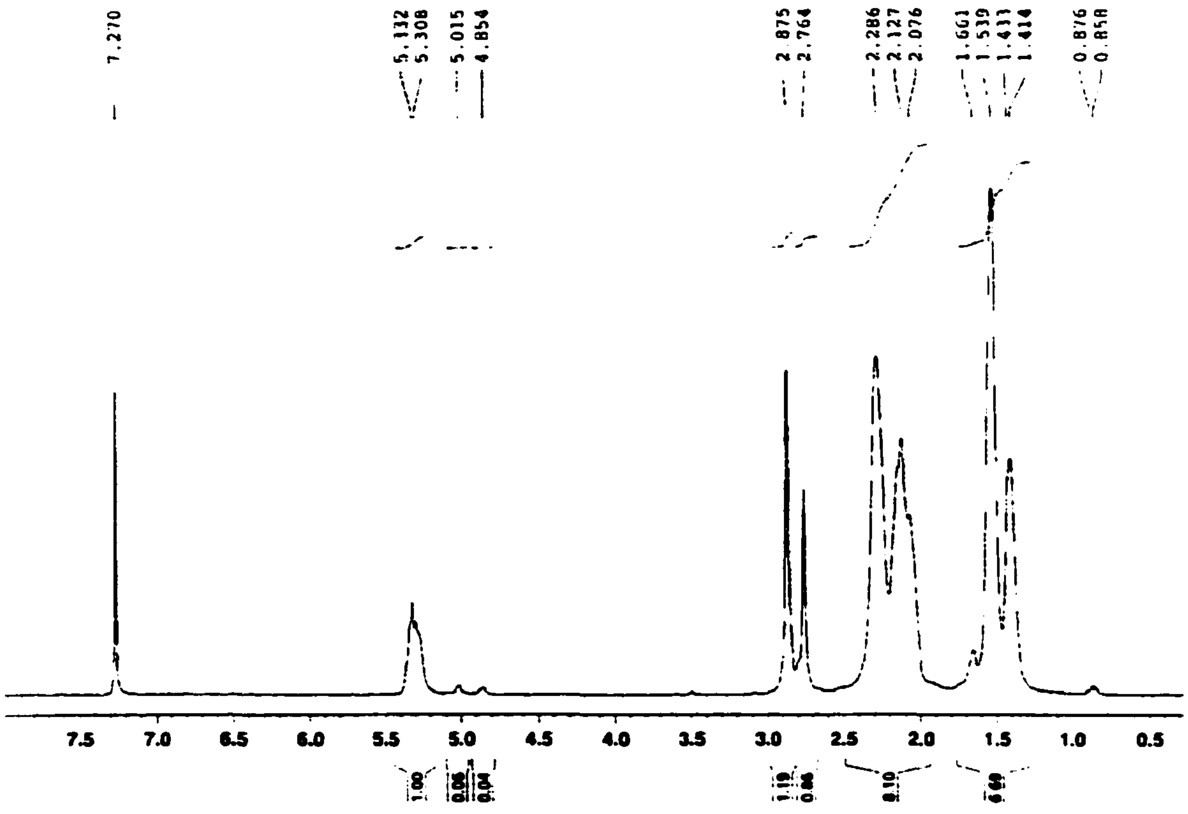
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**1**).



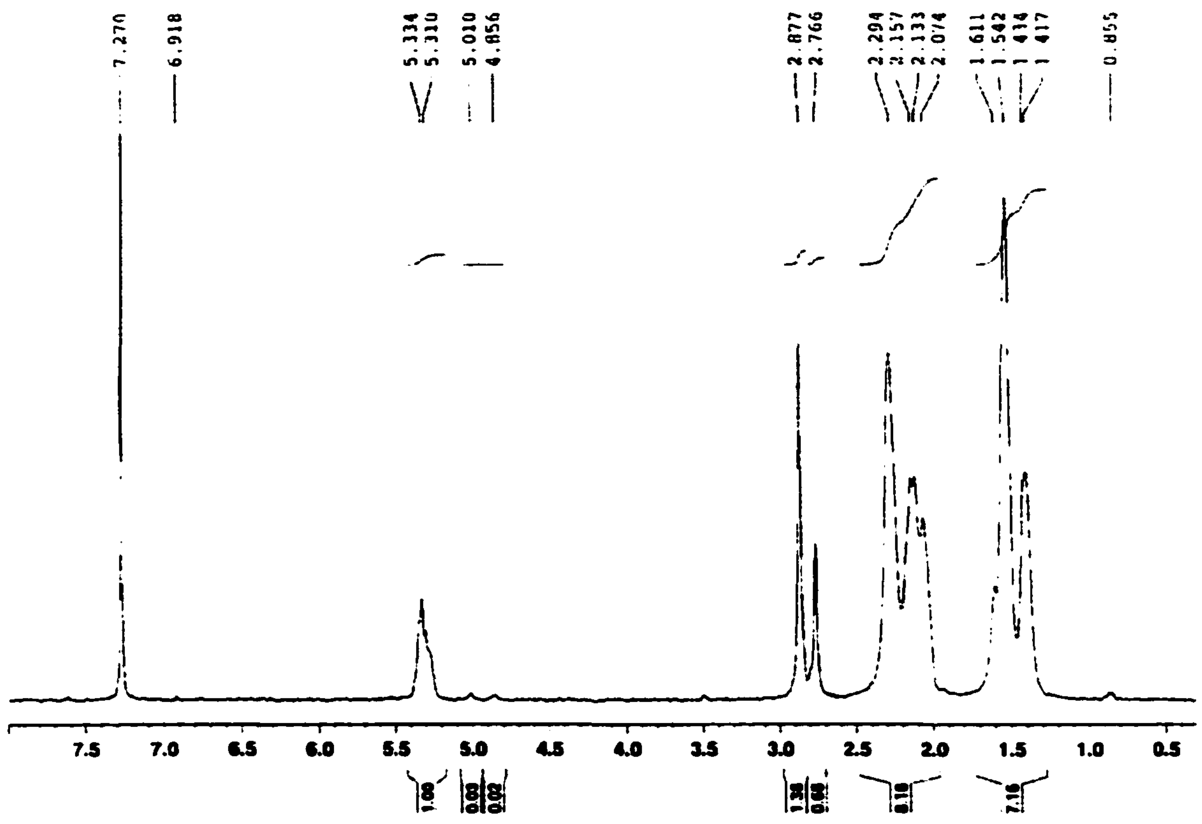
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**2**).



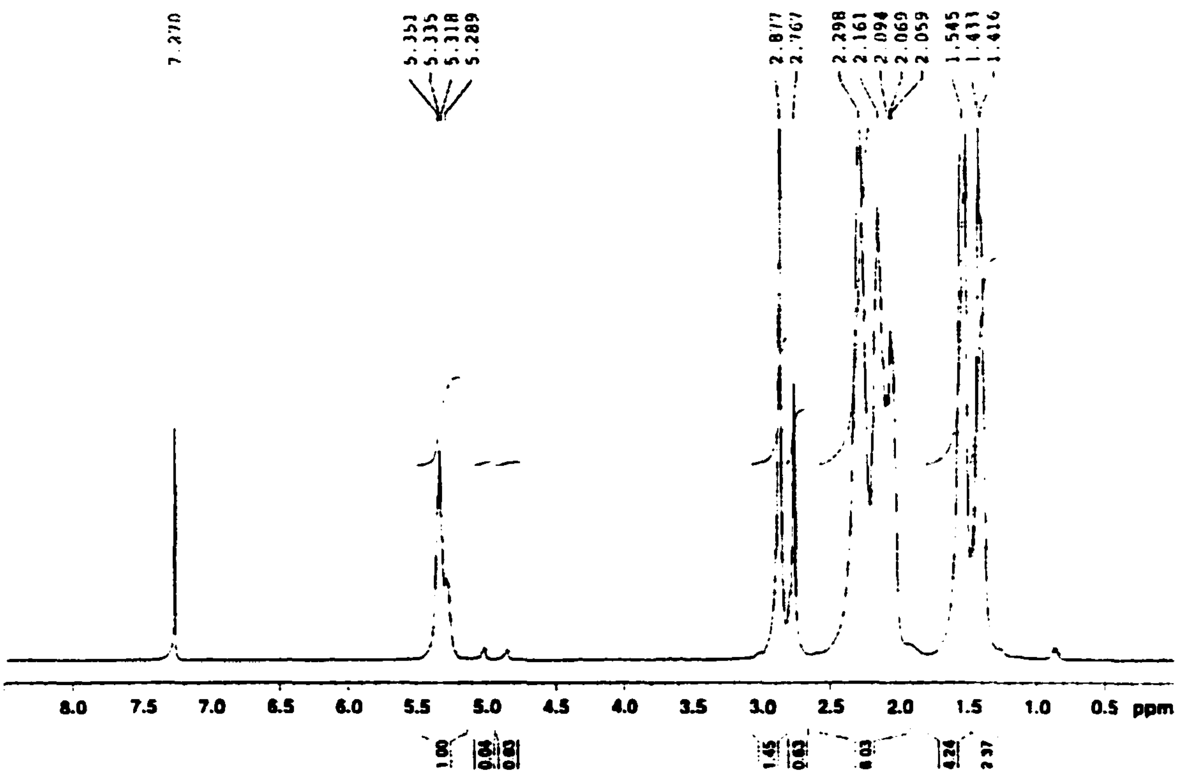
^{13}C NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**2**).



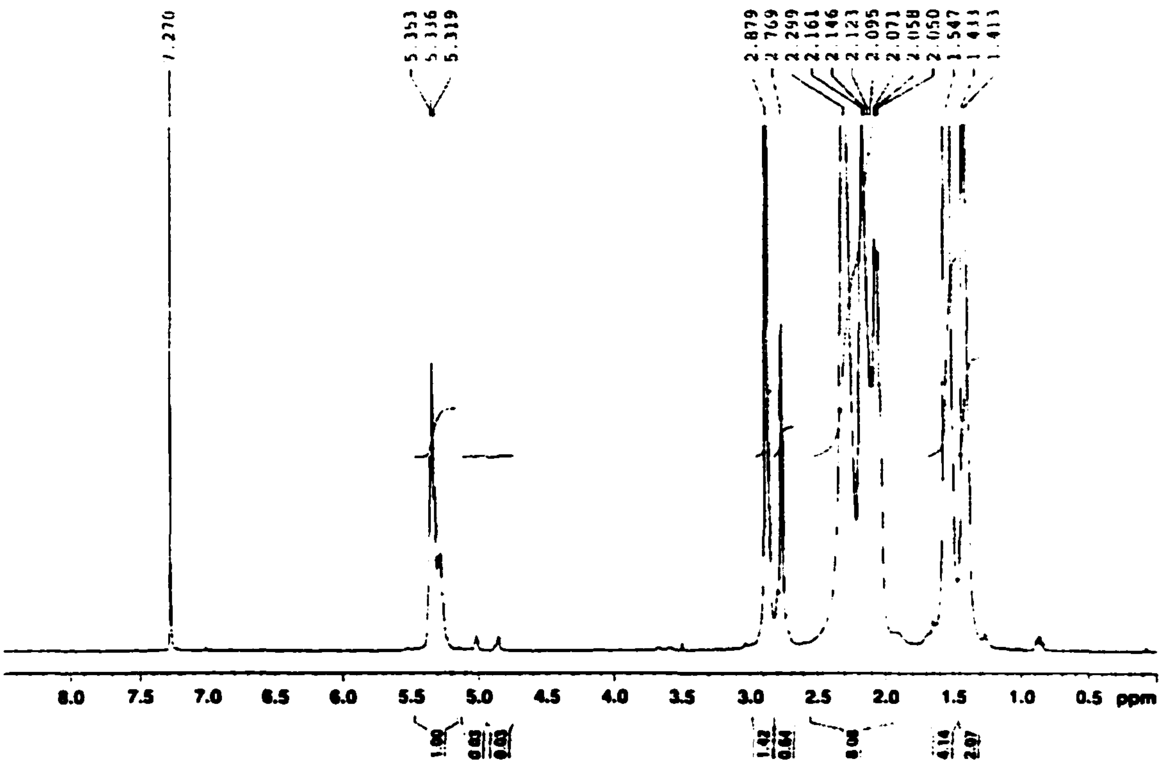
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**3**).



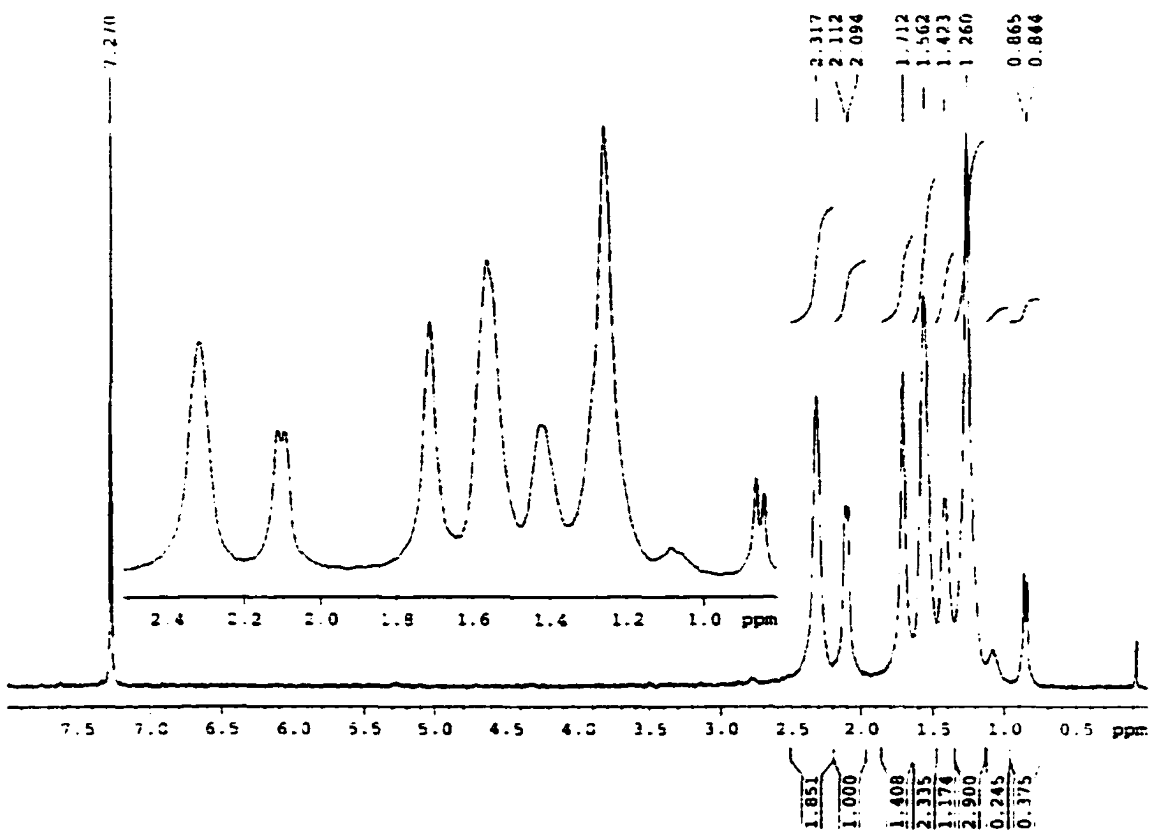
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**4**).



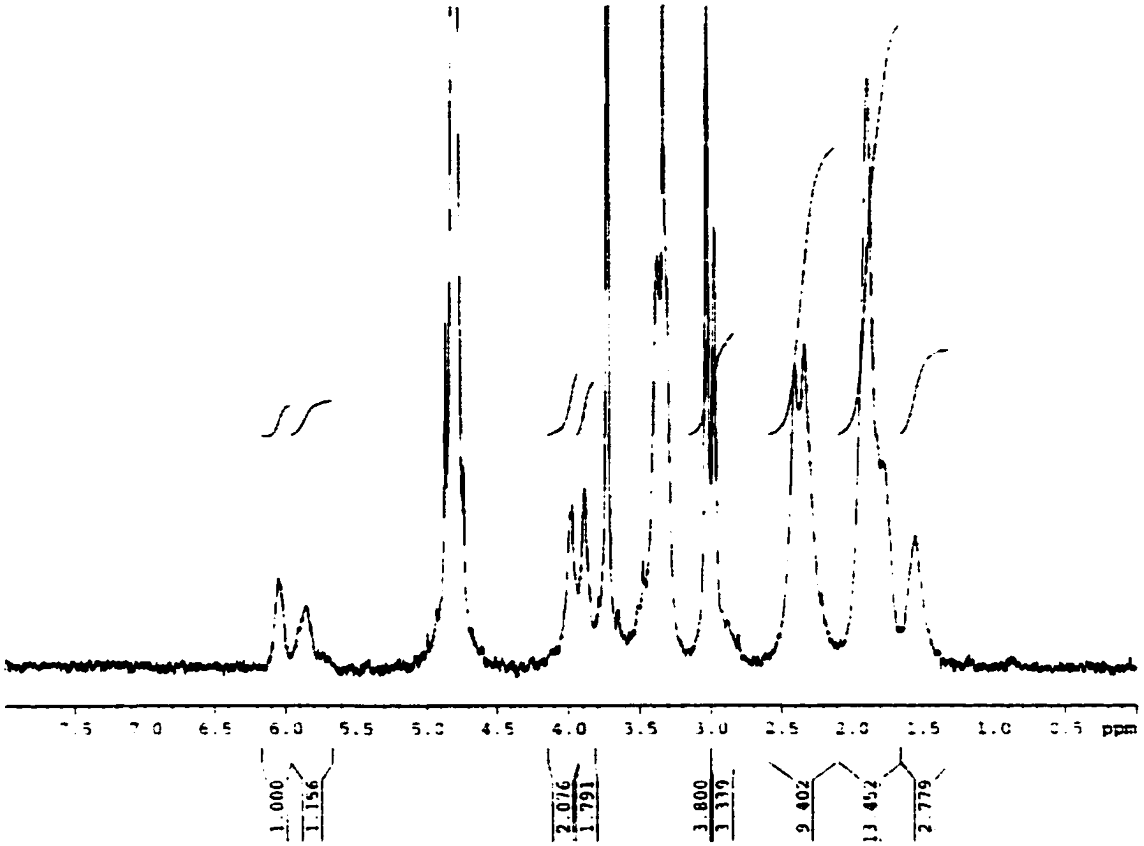
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (5).



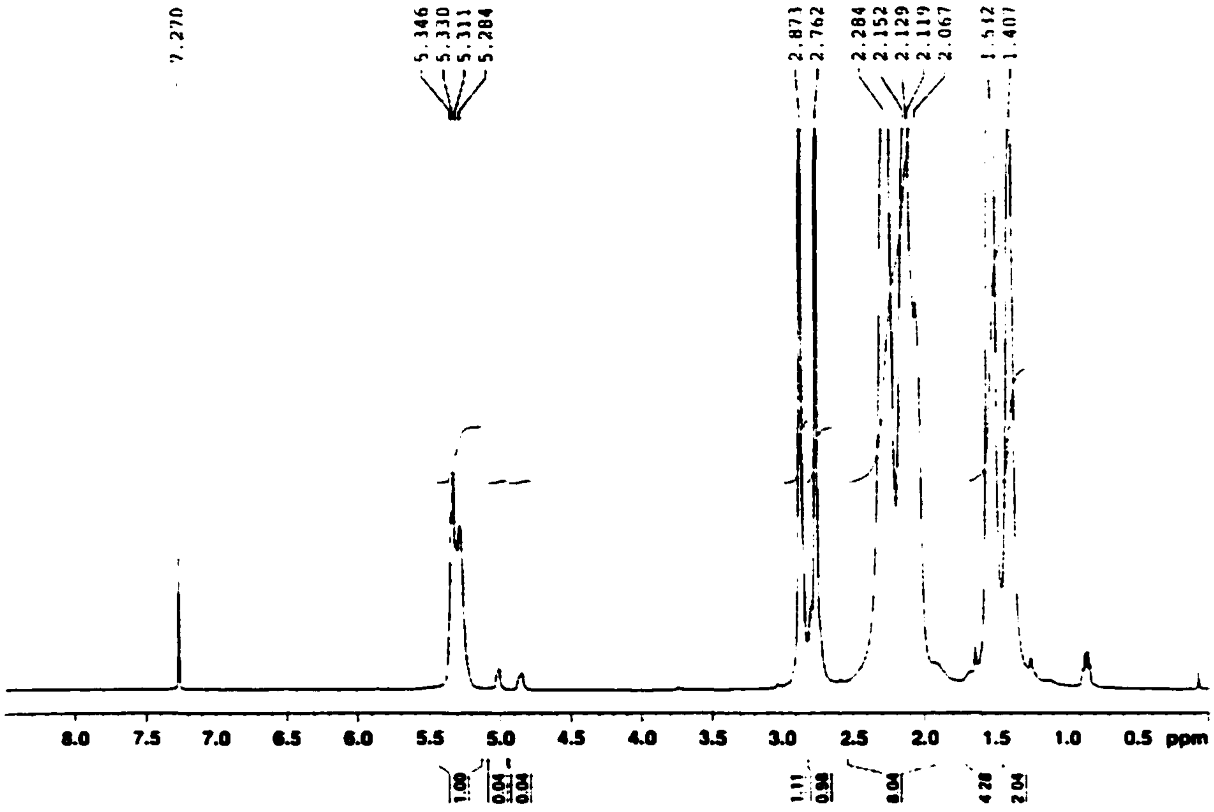
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**6**).



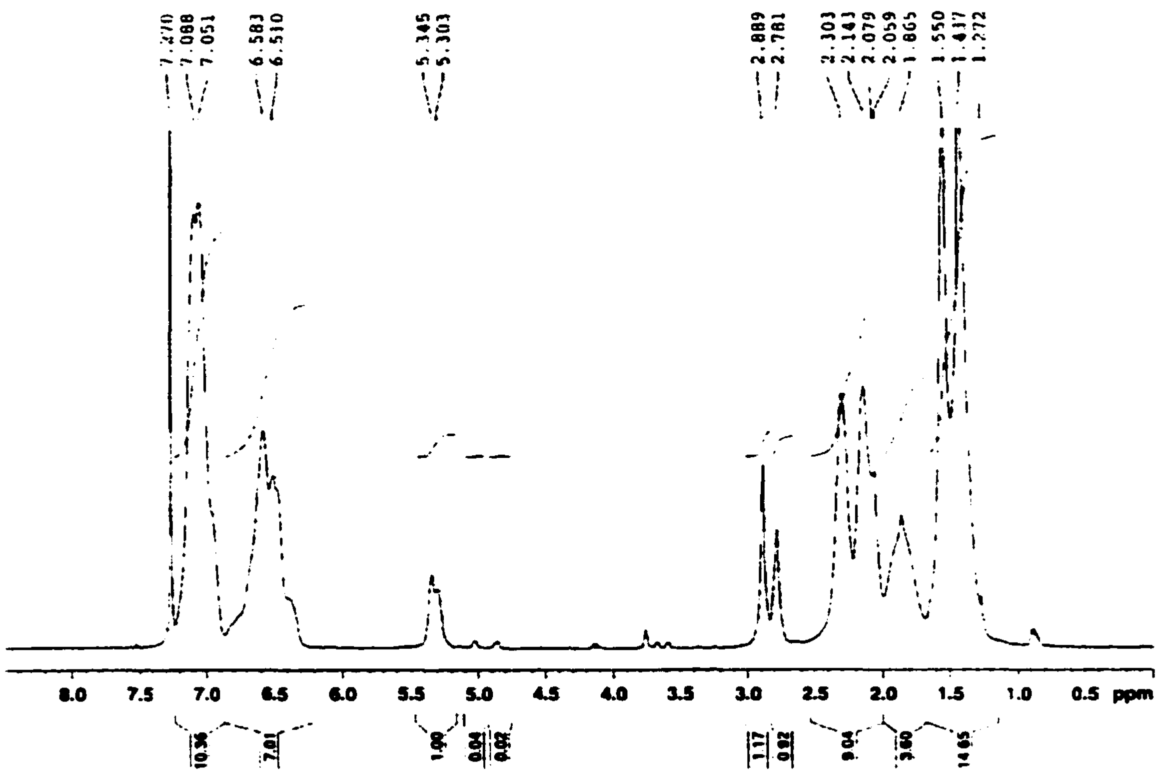
^{1}H NMR of Hydrogenated Poly[2-(*N*-piperidylmethyl)-1,3-butadiene].



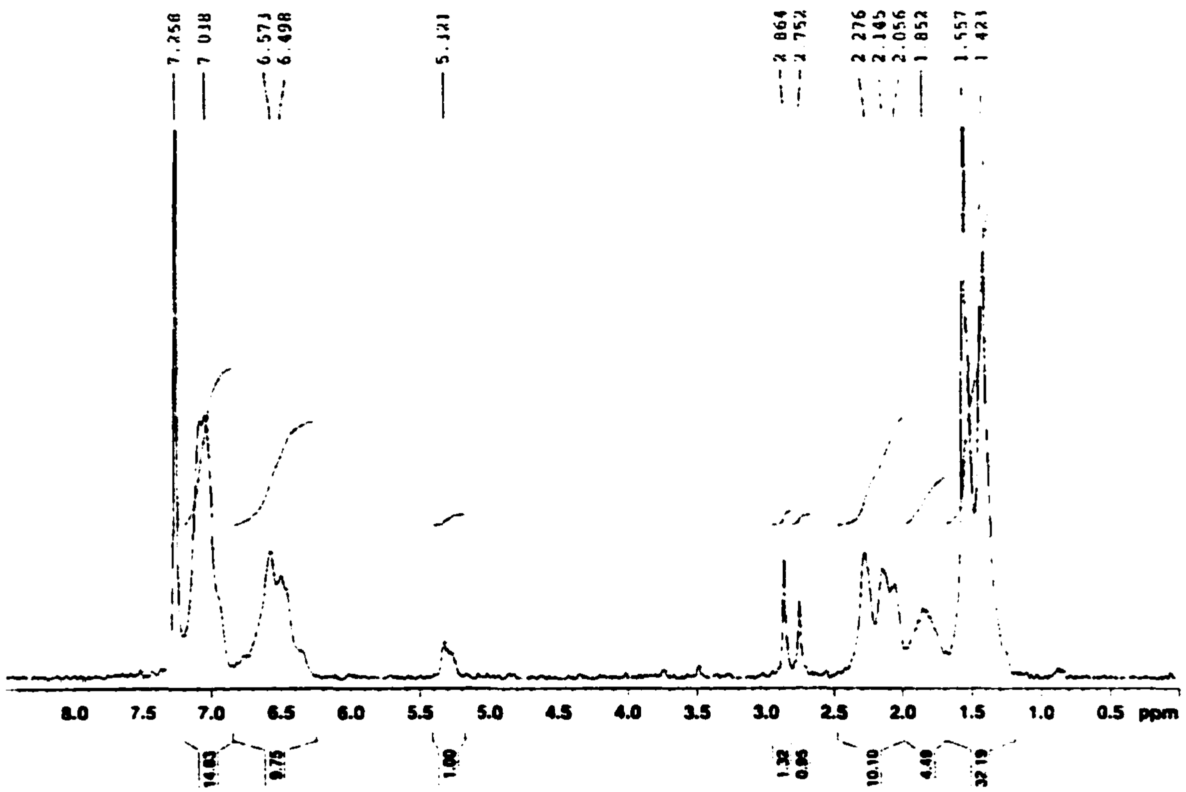
^{1}H NMR of Quaternized Poly[2-(*N*-piperidylmethyl)-1,3-butadiene].



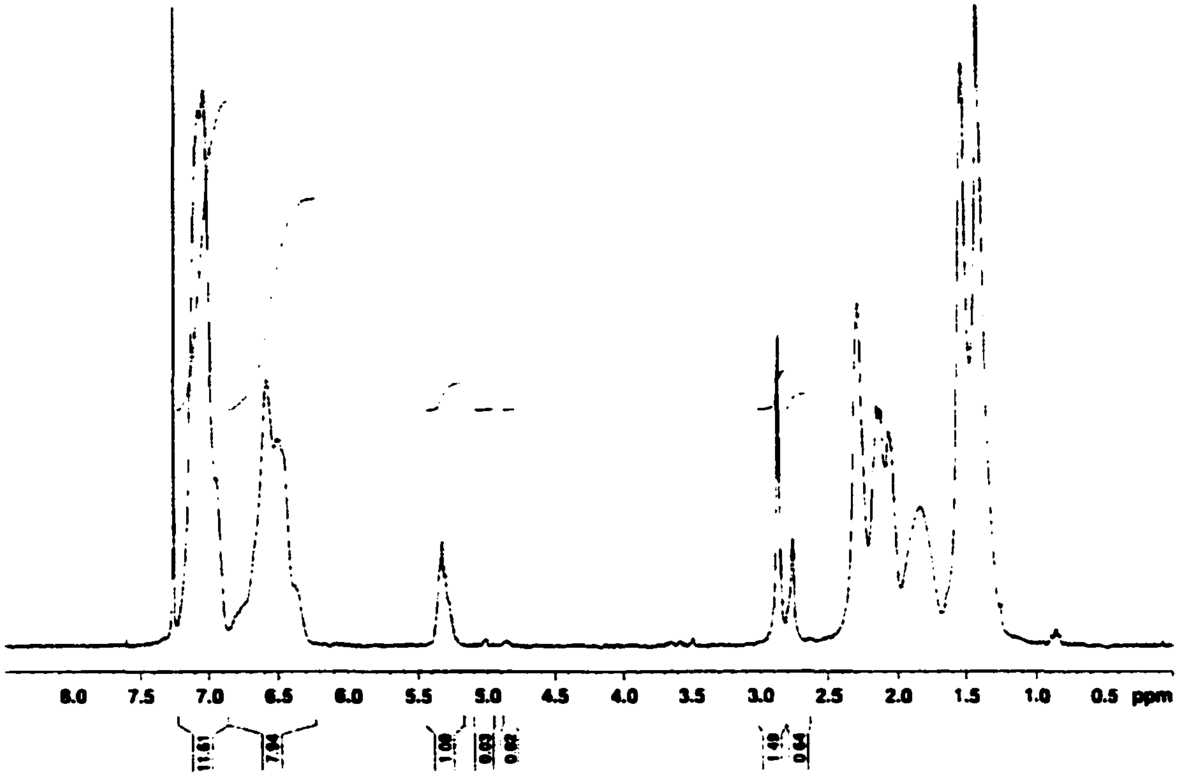
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (7) block 1.



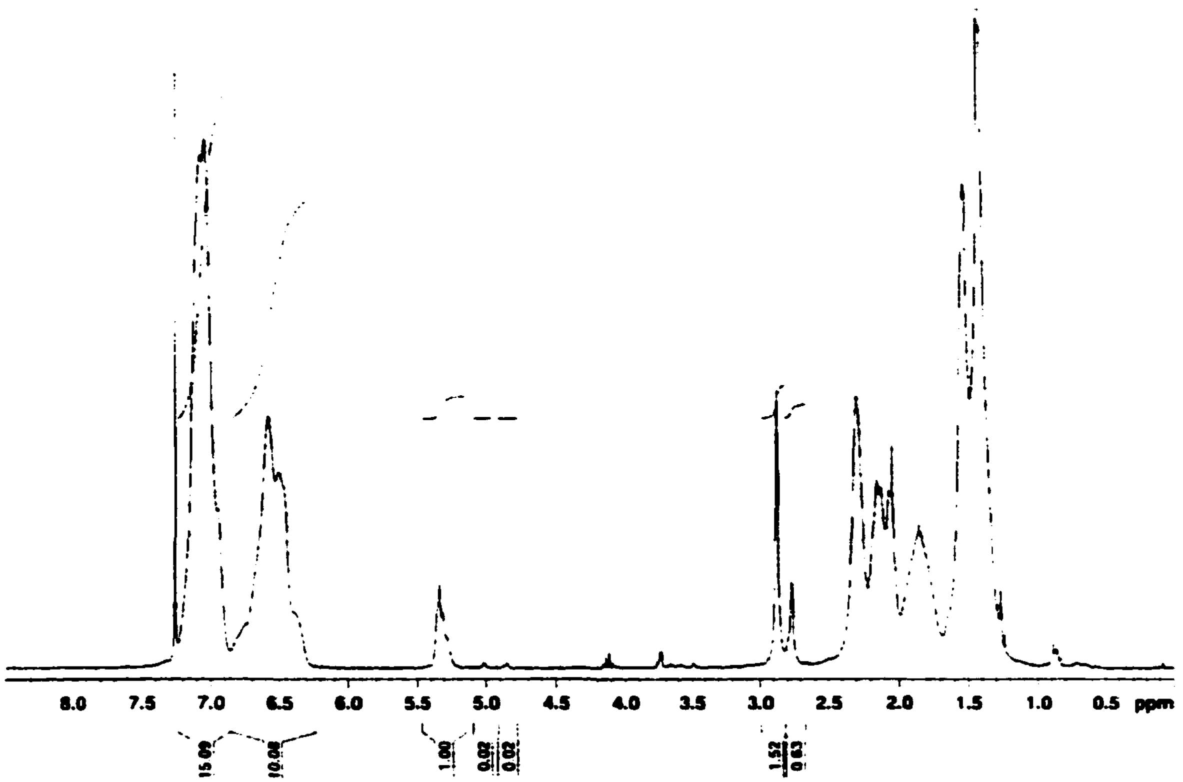
^{1}H NMR of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-co-styrene] (7) block 2.



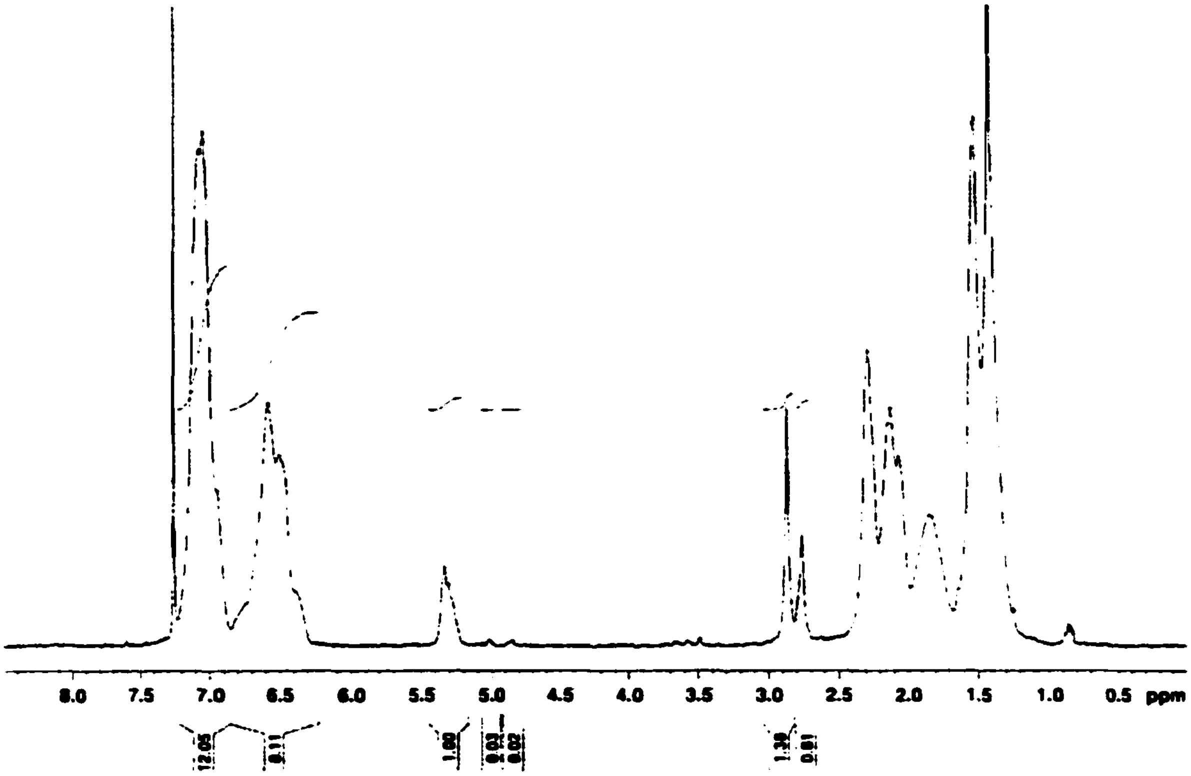
^{1}H NMR of Poly(PMB-*b*-styrene) (8).



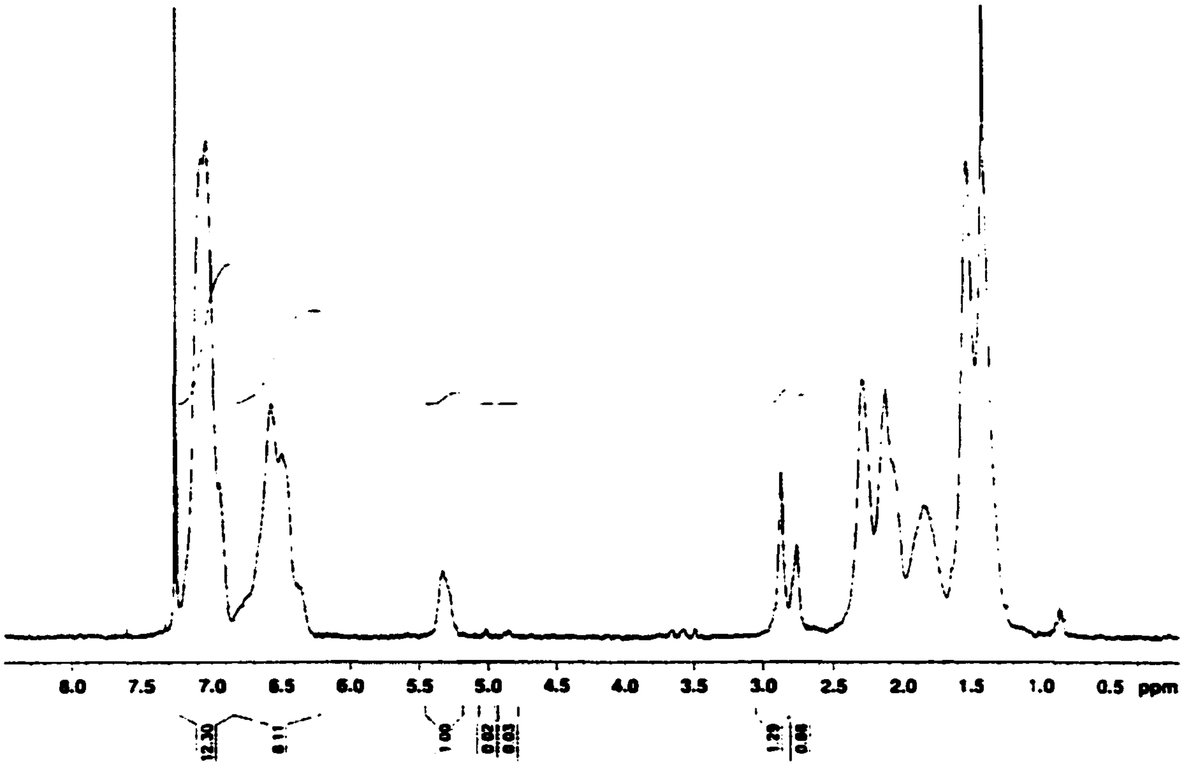
^{1}H NMR of Poly(PMB-*b*-styrene) (**9**).



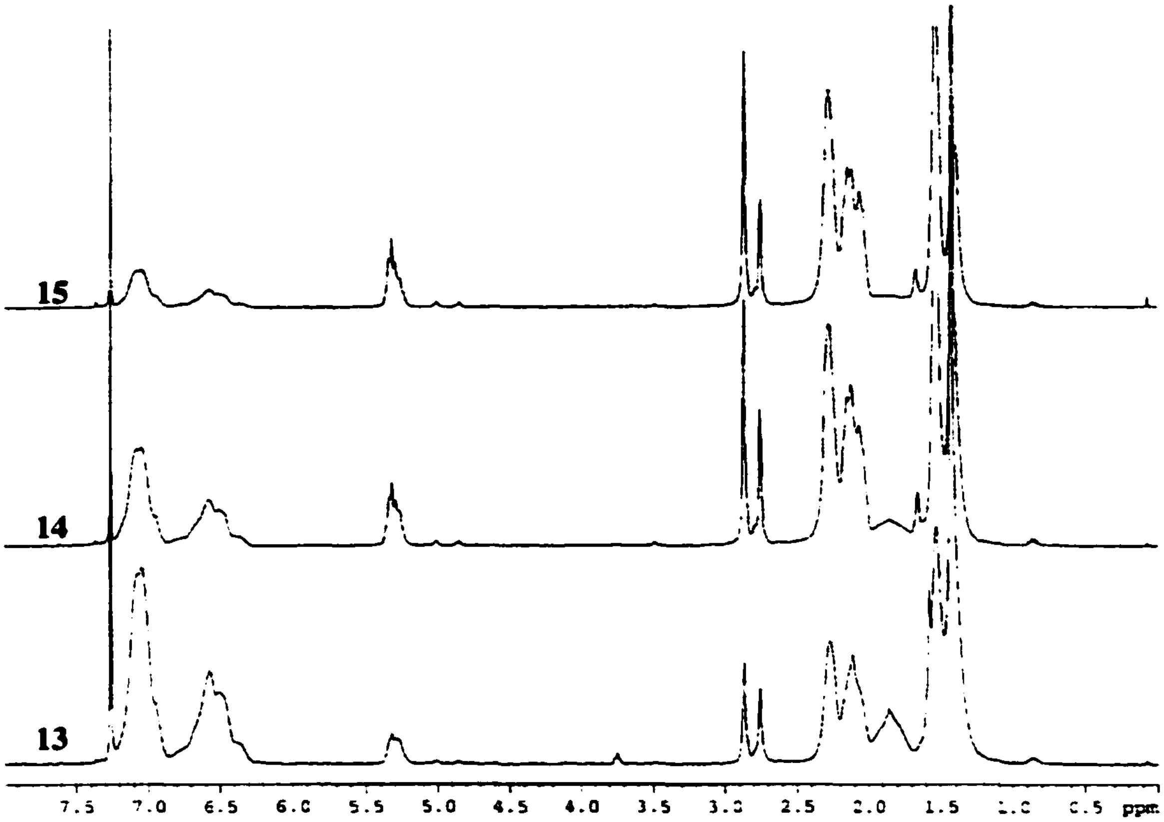
^{1}H NMR of Poly(PMB-*b*-styrene) (**10**).



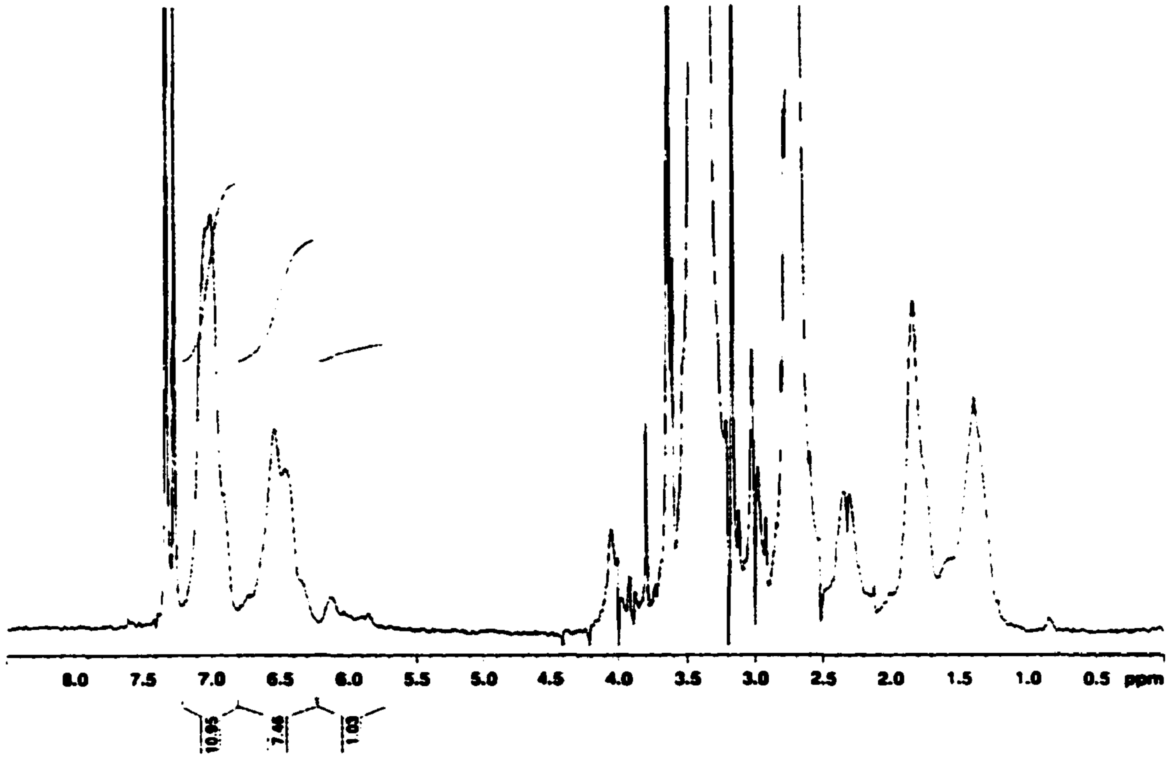
^{1}H NMR of Poly(PMB-*b*-styrene) (**11**).



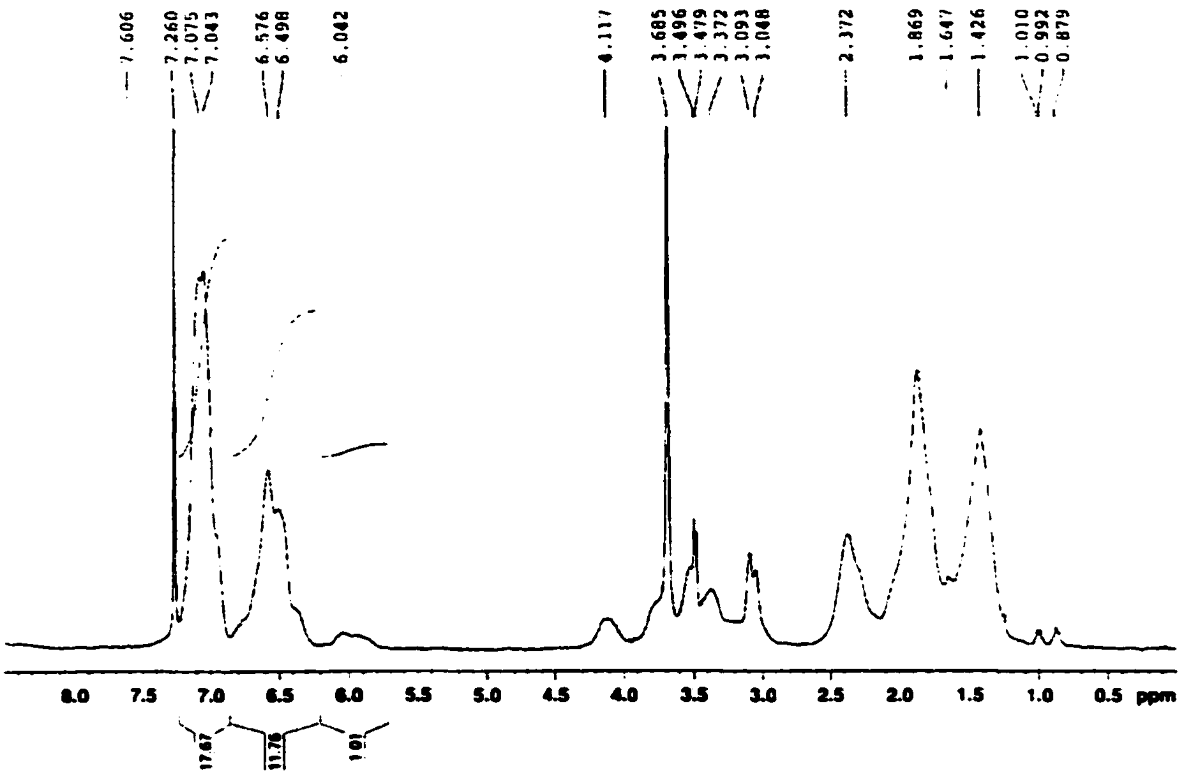
^{1}H NMR of Poly(PMB-*b*-styrene) (**12**).



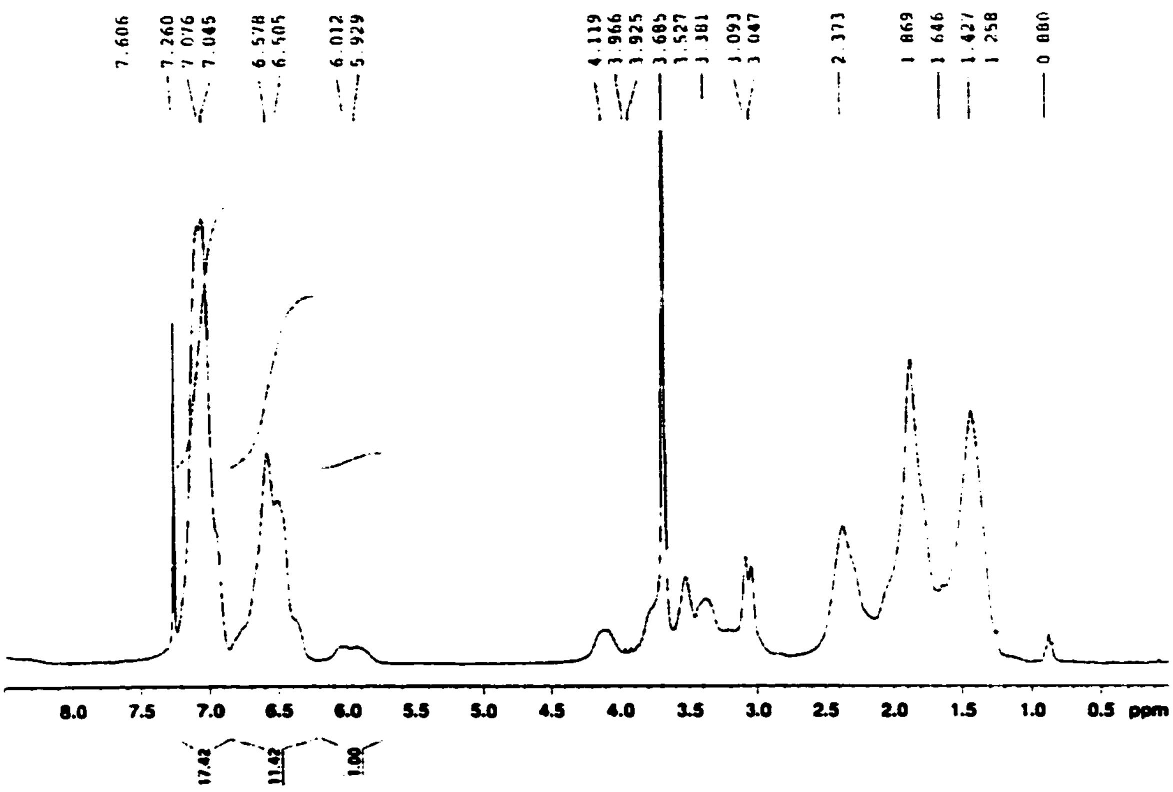
^{1}H NMR of Poly(PMB-*b*-styrene), 13 30% PMB, 14 60% PMB, 15 80% PMB.



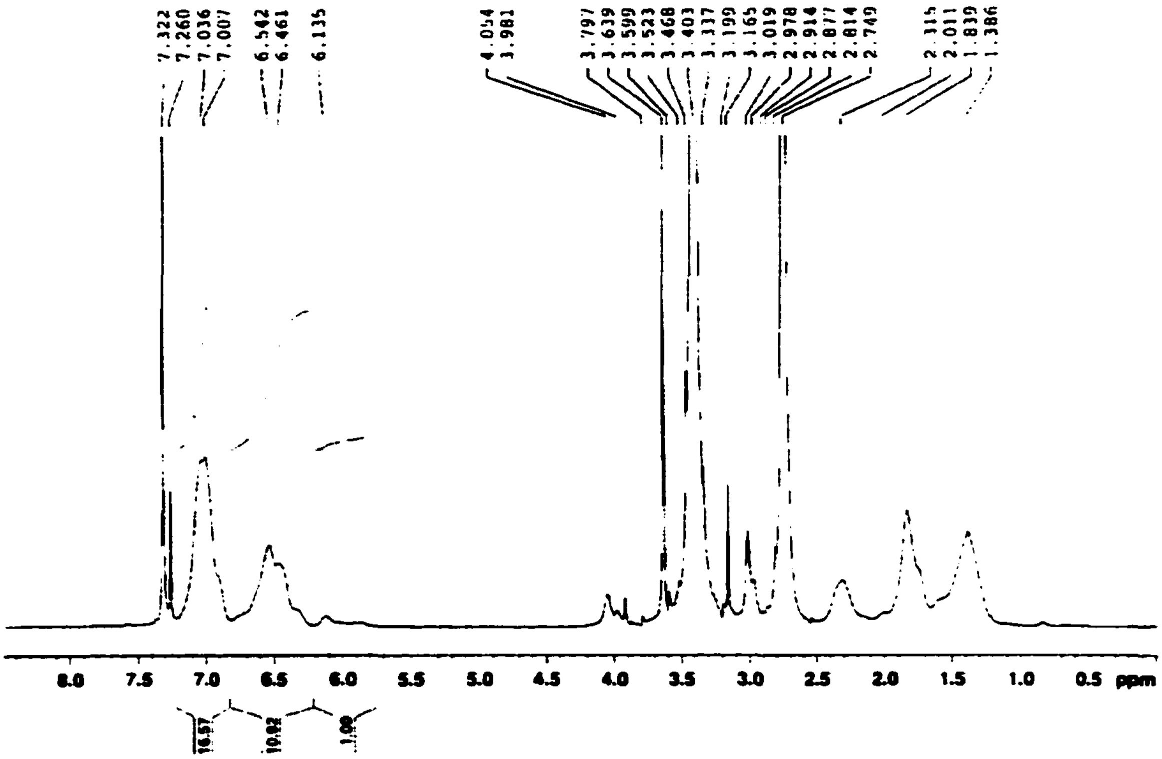
^{1}H NMR of quaternized **9**.



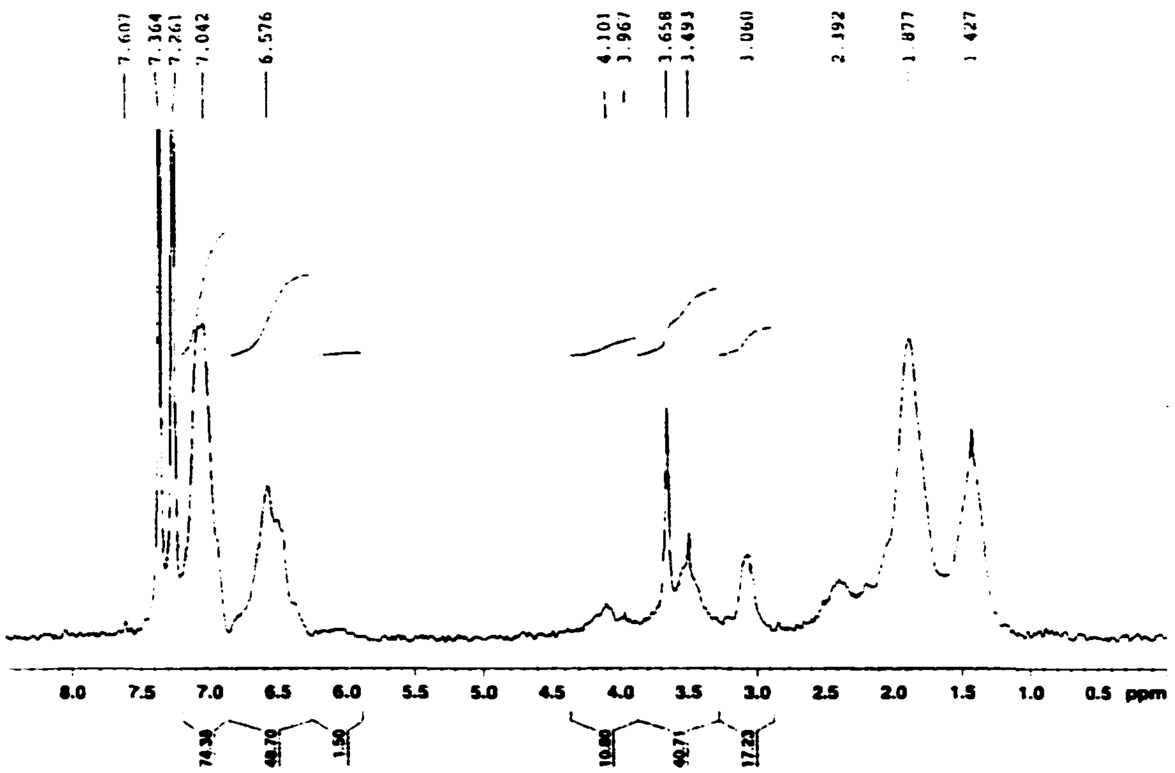
^{1}H NMR of quaternized **10**.



^{1}H NMR of quaternized **11**.



^{1}H NMR of quaternized **10**.



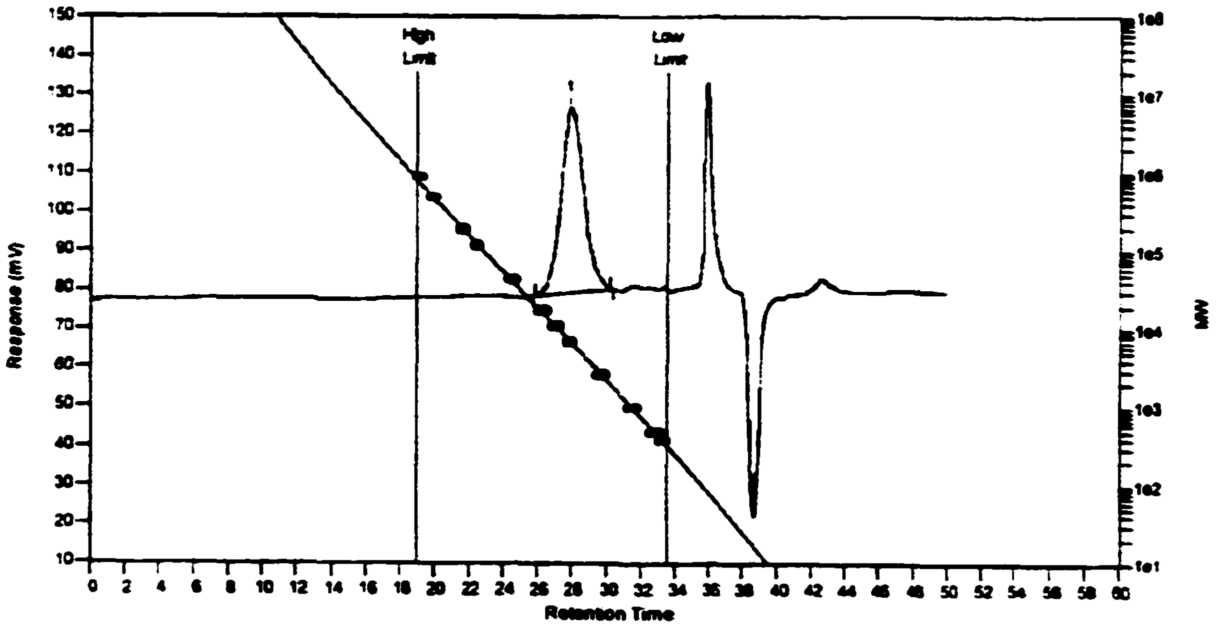
^{1}H NMR of quaternized 7.

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7033	6310	7103	7942	8833	6981	1.12567

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	25.92	27.92	30.18	47.3247	4539.2



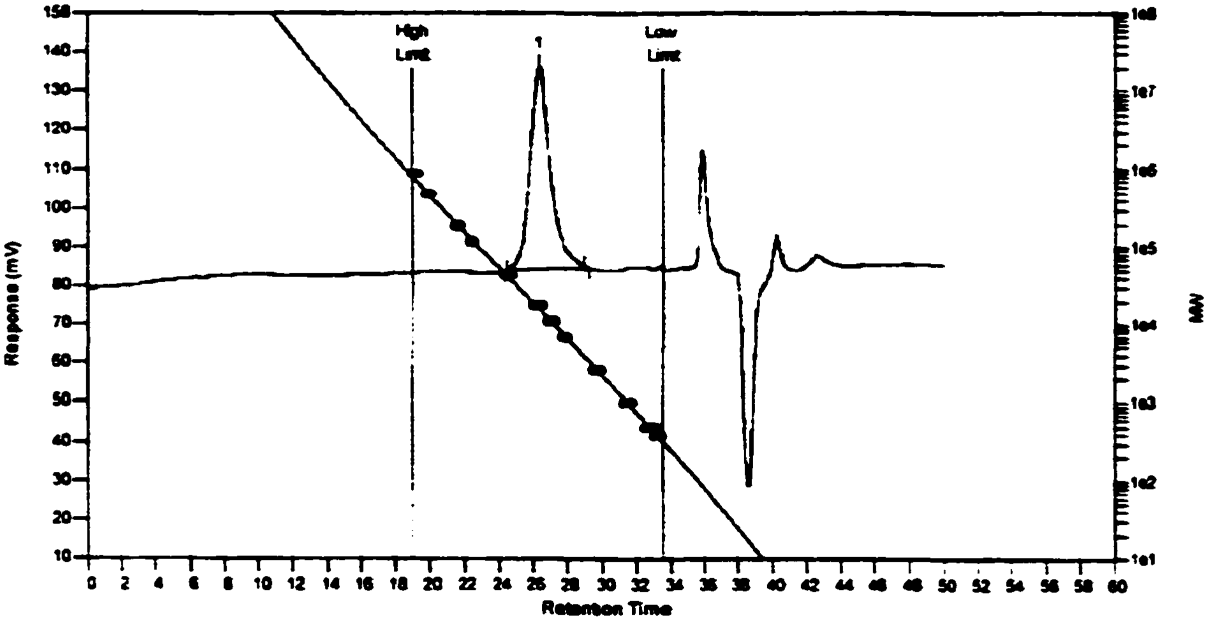
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**1**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	16083	13987	15819	17591	19391	15554	1.13098

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	24.50	26.33	28.95	52.424	4432.72



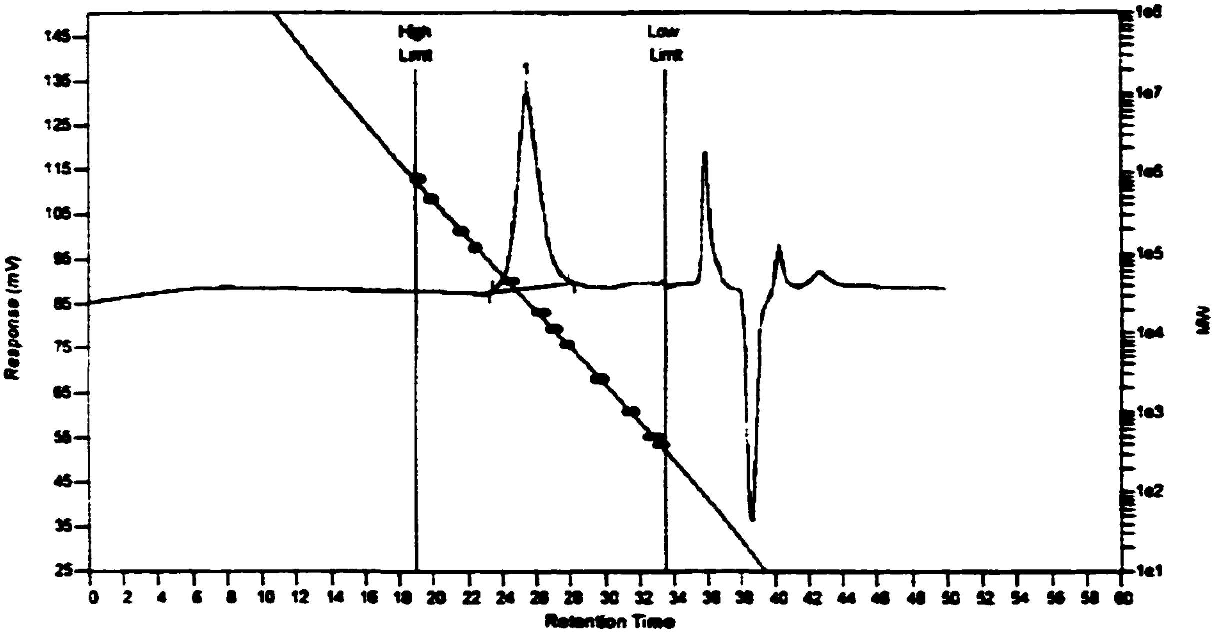
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**2**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25606	22081	25293	28662	32266	24807	1.14546

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	23.45	25.45	27.98	43.9478	4174.25



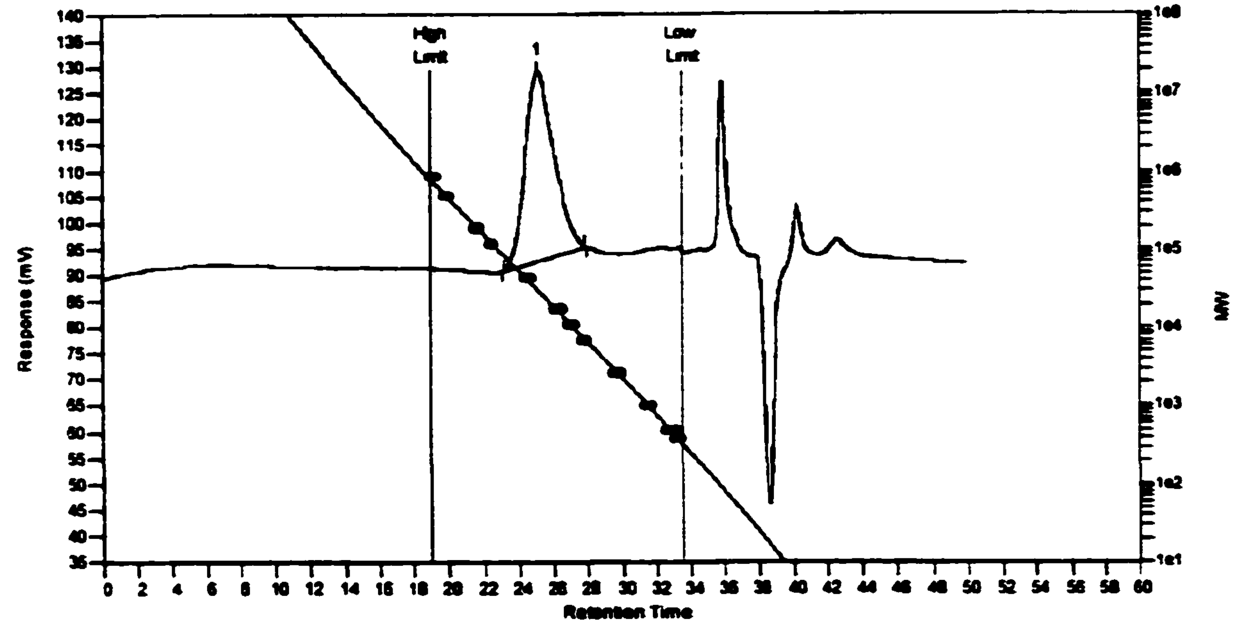
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (3).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	31058	25032	29844	34642	39194	29131	1.19223

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	23.17	25.08	27.85	38.5366	4332.38



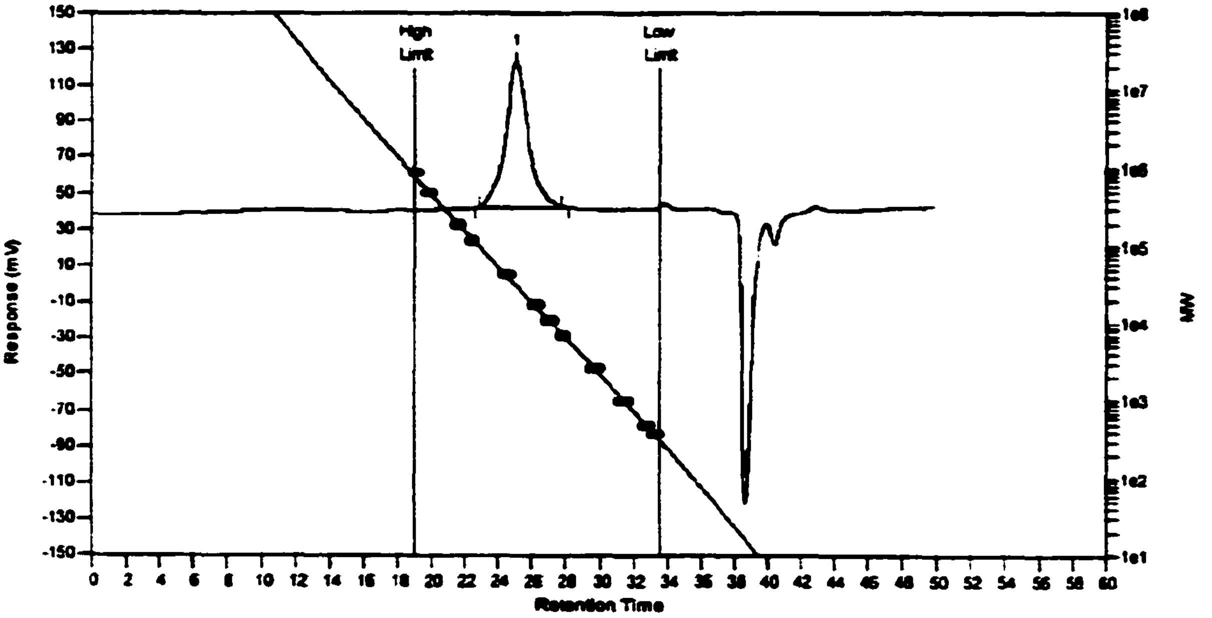
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (4).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	31608	27969	32681	37942	43956	31947	1.16847

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	22.88	25.05	27.77	80.8625	7796.76



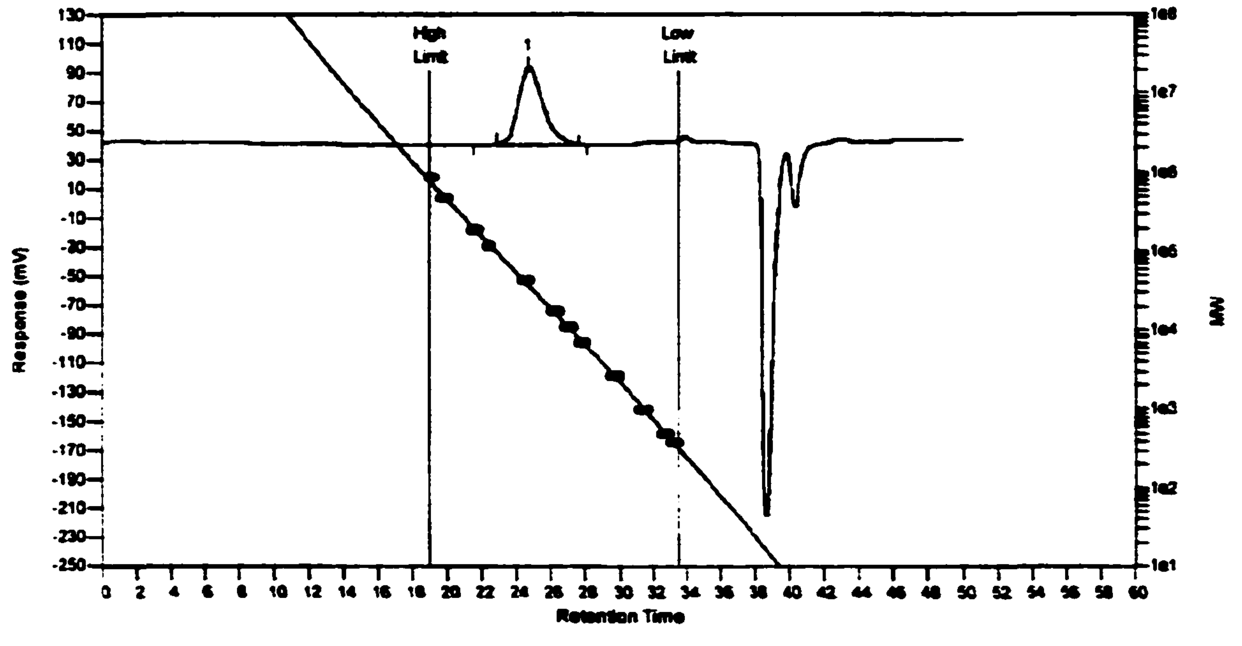
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**5**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	37018	31233	36352	41267	46042	35613	1.1639

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	22.93	24.75	27.70	54.4414	5544.14



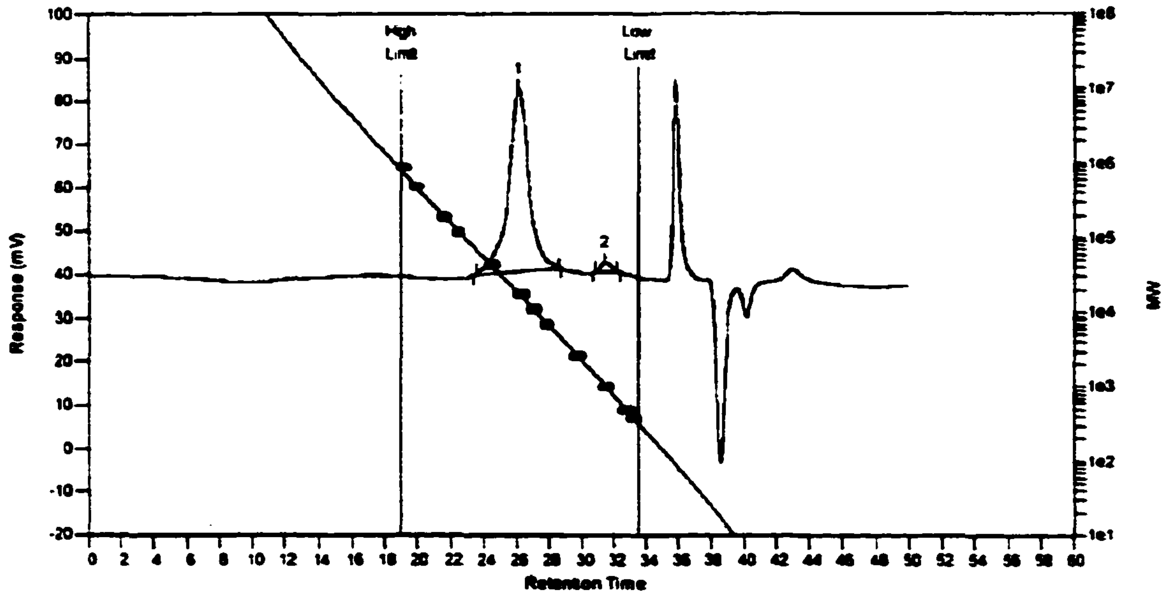
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (**6**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18346	17155	19912	23507	28367	19448	1.16071
2	1057	1012	1019	1055	1080	1010	1.00692

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	23.53	26.08	28.58	42.2262	3743.35
2	30.88	31.43	32.22	2.36202	110.722



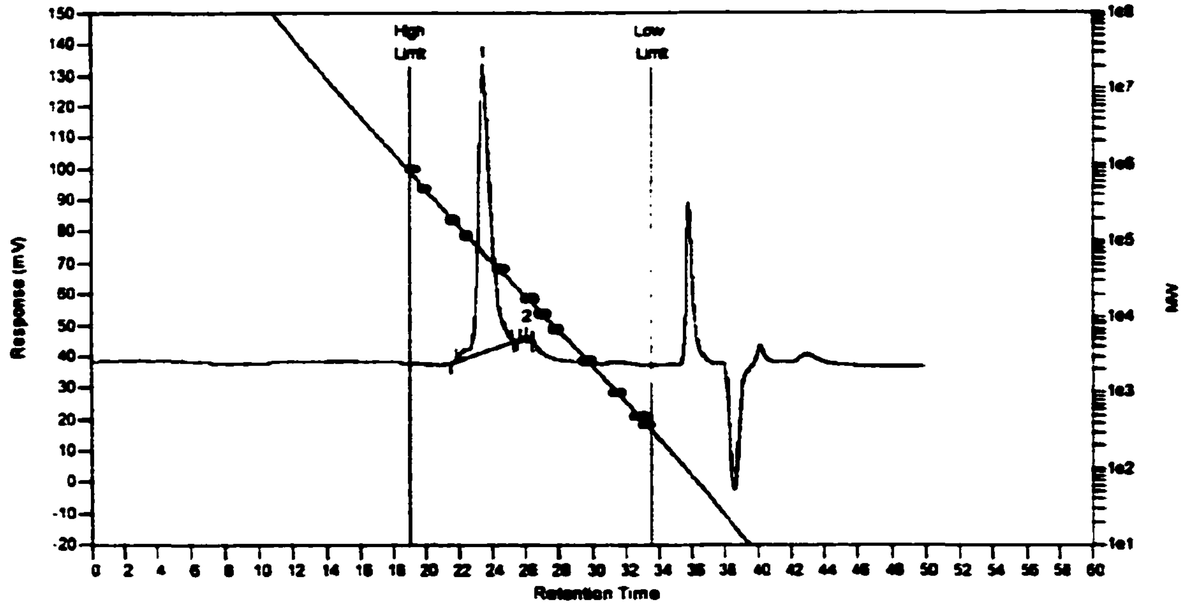
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene] (7) block 1.

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	72846	65664	69777	73966	78729	69168	1.05909
2	18508	18798	18078	18845	18783	17878	0.961698

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	21.88	23.47	25.22	89.2332	4950.64
2	25.75	26.07	26.47	1.37709	41.3679



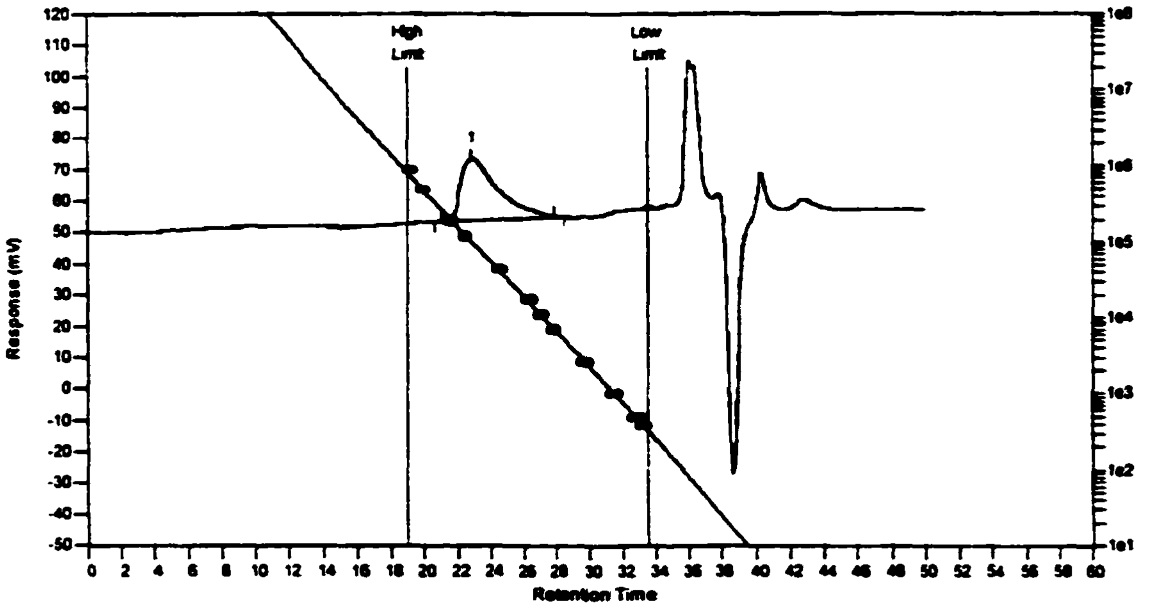
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (7) block 2.

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	100966	49414	77055	99486	118130	73425	1.55936

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	21.05	22.85	27.85	19.5829	3101.65



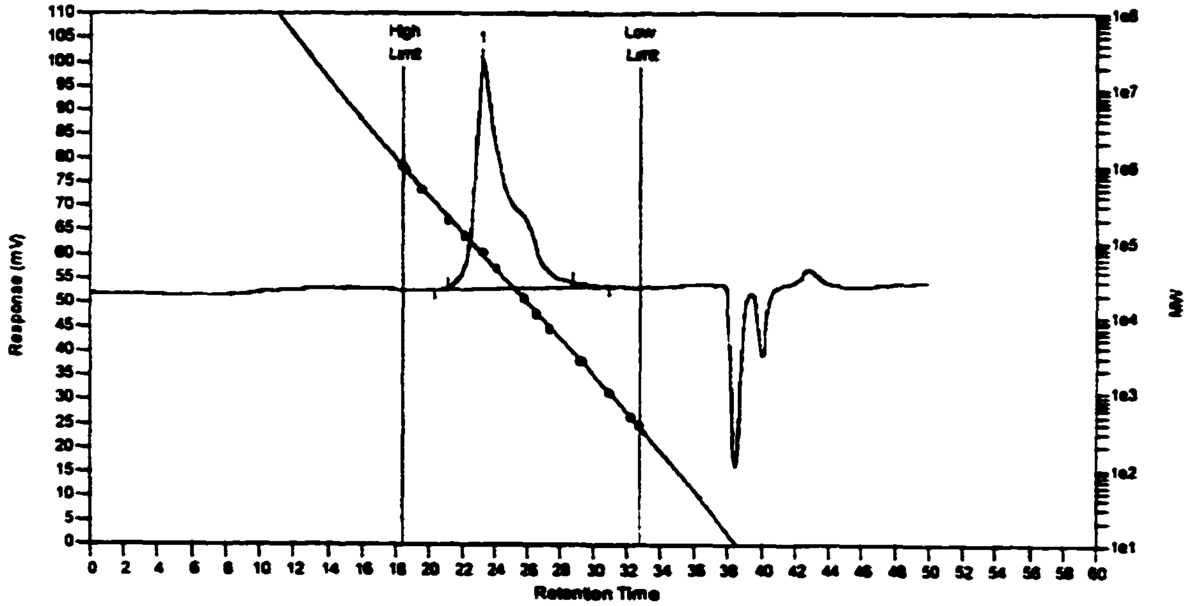
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**8**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	67096	30146	49825	66600	81246	47185	1.65279

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	21.17	23.25	26.77	47.7067	6634.97



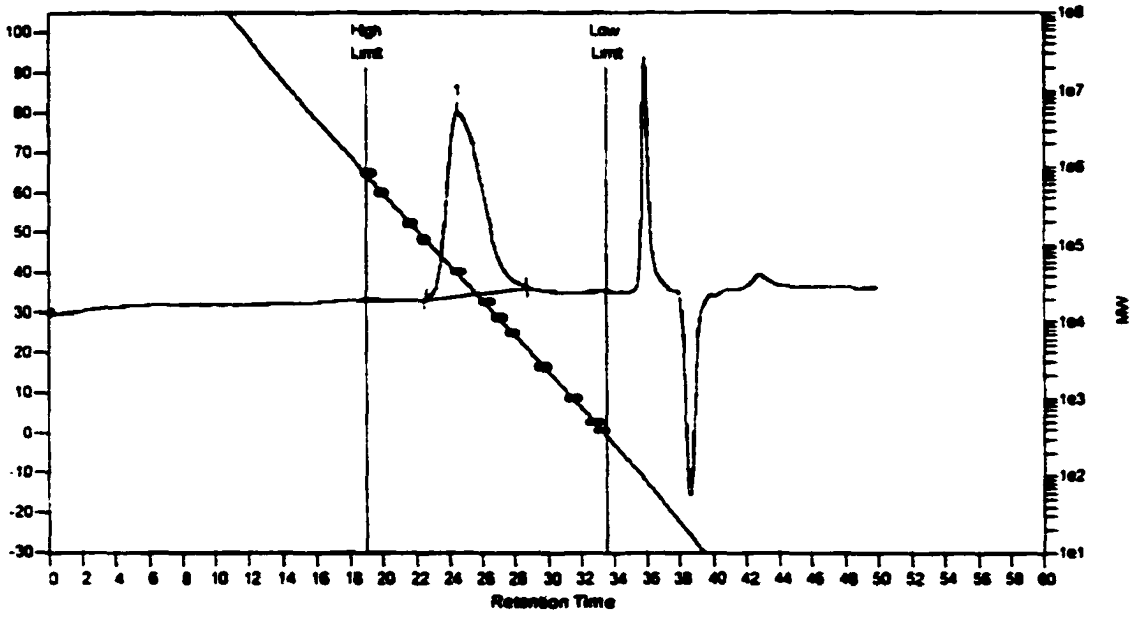
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**9**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	42601	26576	35150	43166	50211	33933	1.32262

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	22.70	24.46	28.67	46.028	6925.71



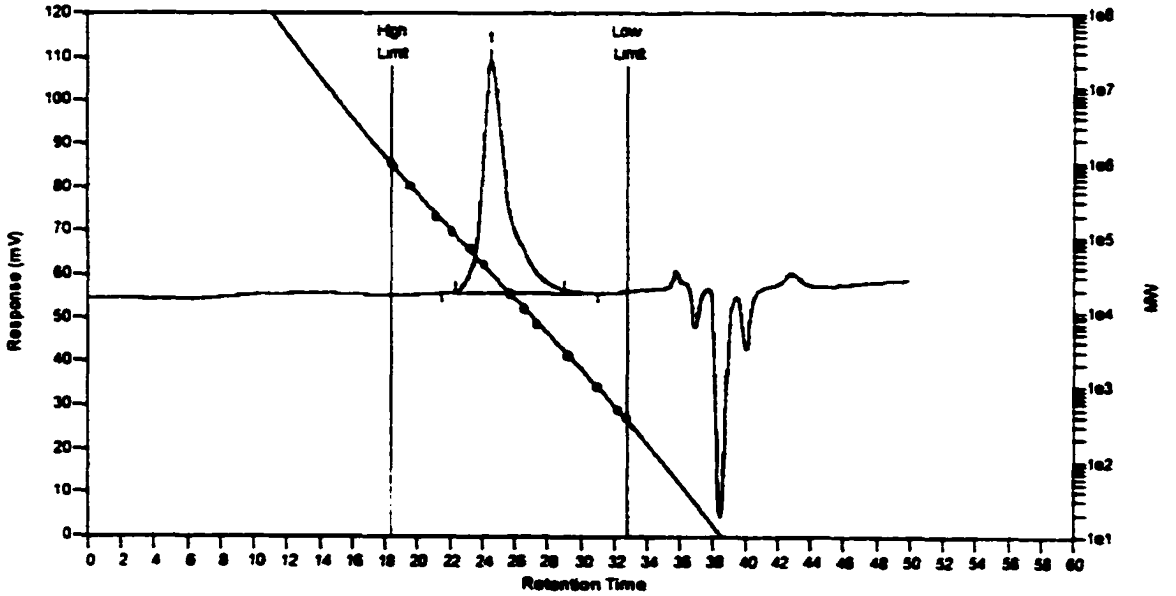
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**10**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	33793	21721	30034	36838	43222	28979	1.38272

Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	22.40	24.53	29.08	53.671	6005.42



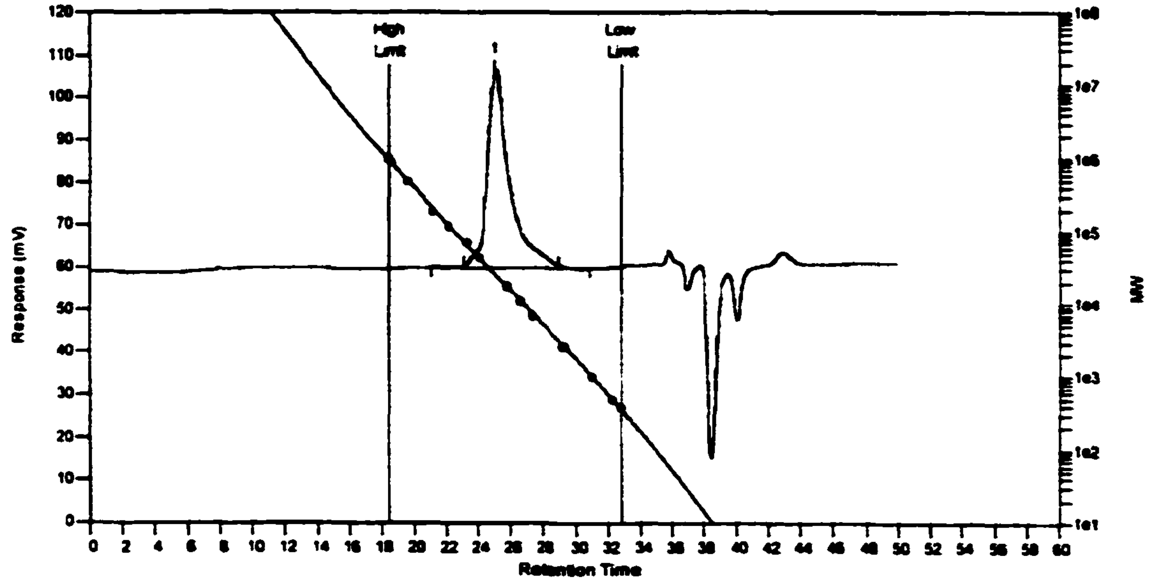
GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**11**).

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	25660	17749	23000	27283	31309	22329	1.29585

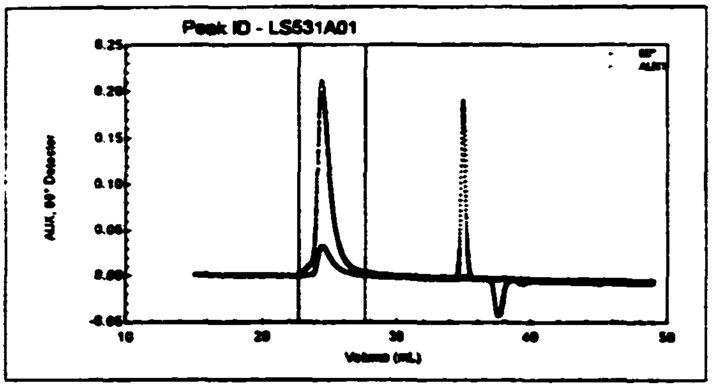
Processed Peaks

Peak No	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	Area (mV.secs)
1	23.12	25.05	28.97	46.7234	4563.14



GPC of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**12**).

File : C:\WTC\ASTRA473\LS531A01.ADF
Sample ID : LS531A
Operator :



COLLECTION INFORMATION

Collection time : Thu May 23, 2002 06:48 AM
Instrument type : DAWN DSP-F
Cell type : K5
Laser wavelength : 632.8 nm
Solvent name : thf
Solvent RI : 1.403
Calibration constants
DAWN : 8.2430e-06
» AUX1 : 2.3233e-04
Flow rate : 1.000 mL/min

PROCESSING INFORMATION

Processing time : Thu May 23, 2002 04:36 PM
DAWN/AUX1 delay : 0.242 mL
Fit method / model : Debye
Calculation method : AUX Constant + 100% mass
Detectors used : 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

RESULTS

PEAK #1
Volume (mL) : 22.658 - 27.550
Slices : 588
A2 (mol mL/g²) : 0.000e+00
Fit degree : 1
Injected Mass (g) : 2.0800e-04
dn/dc (mL/g) : 0.114
Polydispersity(Mw/Mn) : 1.045±0.012 (1.1%)
Polydispersity(Mz/Mn) : 1.127±0.052 (5%)

Molar Mass Moments (g/mol)
Mn : 4.110e+04 (0.8%)
Mw : 4.296e+04 (0.8%)
Mz : 4.631e+04 (4%)

Light Scattering of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**13**).

```
File                       :  C:\WTC\ASTRA473\LS531B01.ADF
Sample ID                  :  LS531B
Operator                   :
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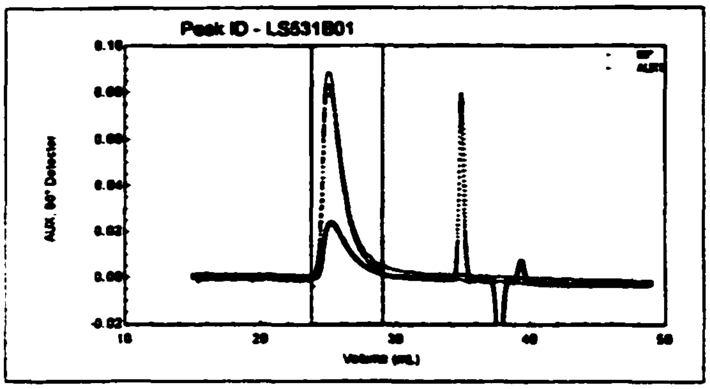
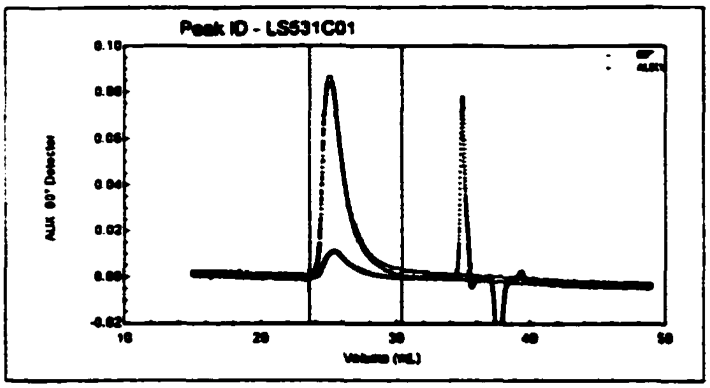


```
COLLECTION INFORMATION

Collection time            :  Thu  May 23, 2002  07:41 AM
Instrument type            :  DAWN DSP-F
Cell type                  :  K5
Laser wavelength           :  632.8  nm
Solvent name               :  thf
Solvent RI                 :  1.403
Calibration constants
   DAWN                    :  8.2430e-06
 » AUX1                    :  2.3233e-04
Flow rate                  :  1.000 mL/min

PROCESSING INFORMATION

Processing time            :  Thu  May 23, 2002  04:38 PM
DAWN/AUX1 delay            :  0.242 mL
Fit method / model         :  Debye
Calculation method         :  AUX Constant + 100% mass
Detectors used             :  2  3  4  5  6  7  8  9  10 11 12 13 14 15 16 17 18

RESULTS
                              PEAK #1
Volume (mL)                :  23.708 - 28.983
Slices                     :  634
A2 (mol mL/g²)             :  0.000e+00
Fit degree                 :  1
Injected Mass (g)          :  2.1600e-04
dn/dc (mL/g)               :  0.086
Polydispersity(Mw/Mn)      :  1.064±0.016 (1.5%)
Polydispersity(Mz/Mn)      :  1.137±0.027 (2.4%)

Molar Mass Moments (g/mol)
 Mn                        :  4.371e+04 (1.1%)
 Mw                        :  4.653e+04 (1.0%)
 Mz                        :  4.970e+04 (2.1%)
```

Light Scattering of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**14**).

File : C:\WTC\ASTRA473\LS531C01.ADF
Sample ID : LS531C
Operator :



COLLECTION INFORMATION

Collection time : Thu May 23, 2002 09:26 AM
Instrument type : DAWN DSP-F
Cell type : K5
Laser wavelength : 632.8 nm
Solvent name : thf
Solvent RI : 1.403
Calibration constants
DAWN : 8.2430e-06
» AUX1 : 2.3233e-04
Flow rate : 1.000 mL/min

PROCESSING INFORMATION

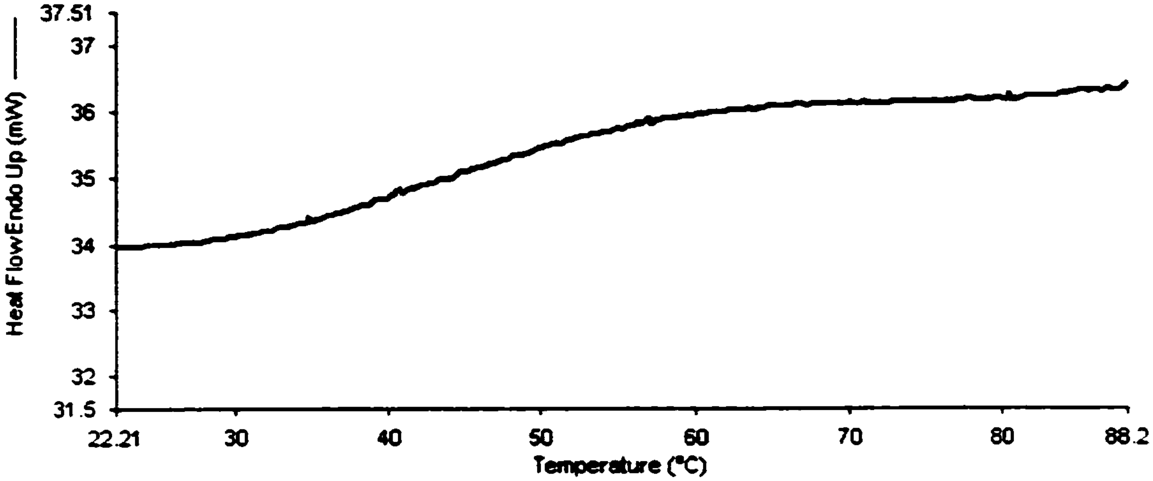
Processing time : Thu May 23, 2002 04:40 PM
DAWN/AUX1 delay : 0.242 mL
Fit method / model : Debye
Calculation method : AUX Constant + 100% mass
Detectors used : 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

RESULTS

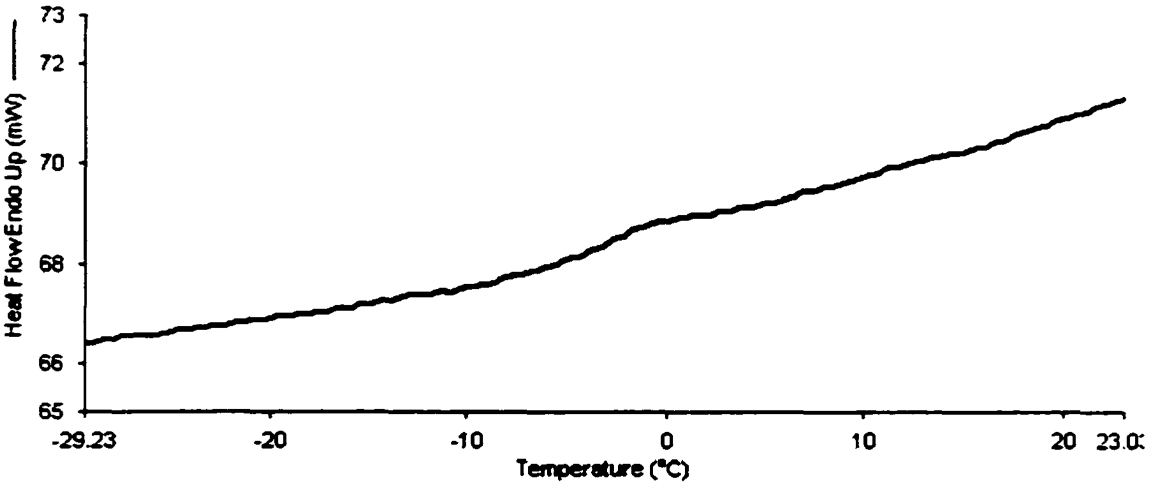
PEAK #1
Volume (mL) : 23.558 - 30.417
Slices : 824
A2 (mol mL/g²) : 0.000e+00
Fit degree : 1
Injected Mass (g) : 2.0400e-04
dn/dc (mL/g) : 0.091
Polydispersity(Mw/Mn) : 1.065±0.019 (1.8%)
Polydispersity(Mz/Mn) : 1.178±0.086 (7%)

Molar Mass Moments (g/mol)
Mn : 4.378e+04 (1.2%)
Mw : 4.662e+04 (1.4%)
Mz : 5.155e+04 (7%)

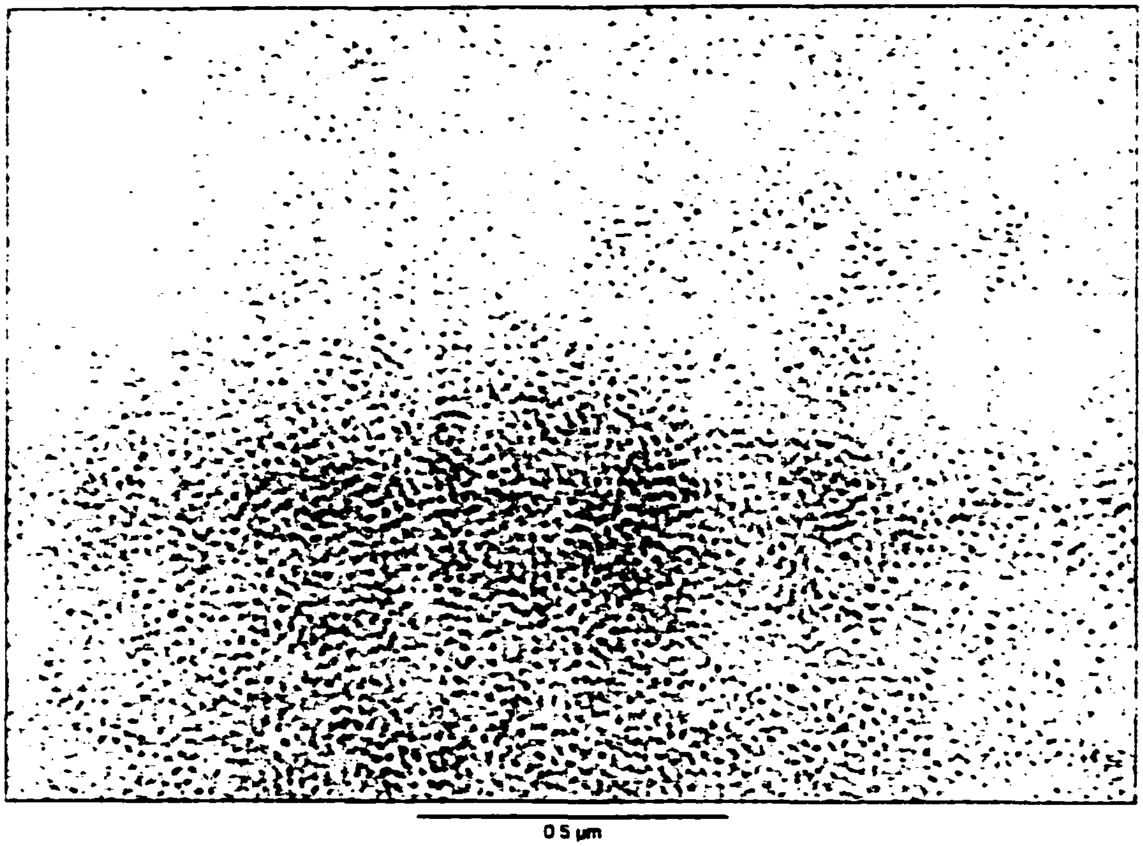
Light Scattering of Poly[2-(*N*-piperidylmethyl)-1,3-butadiene-*b*-styrene] (**15**).



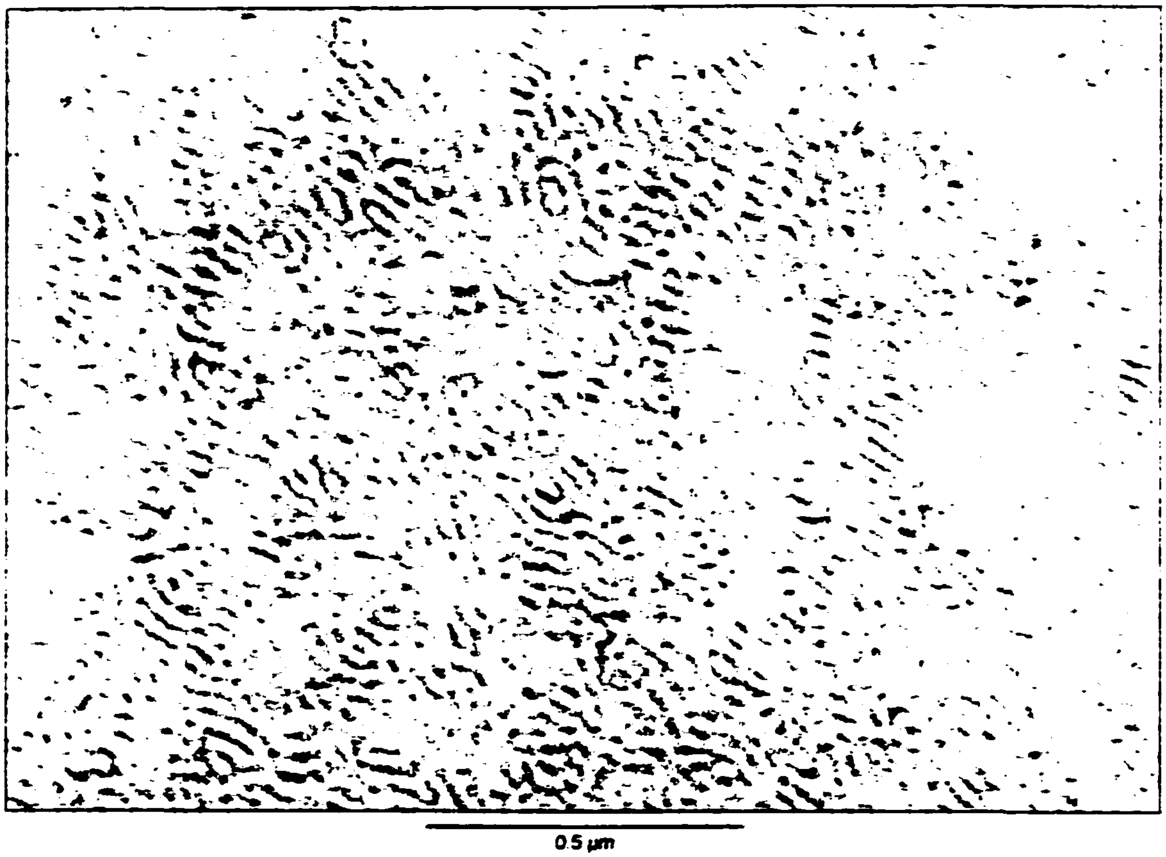
DSC of Quaternized Poly(PMB).



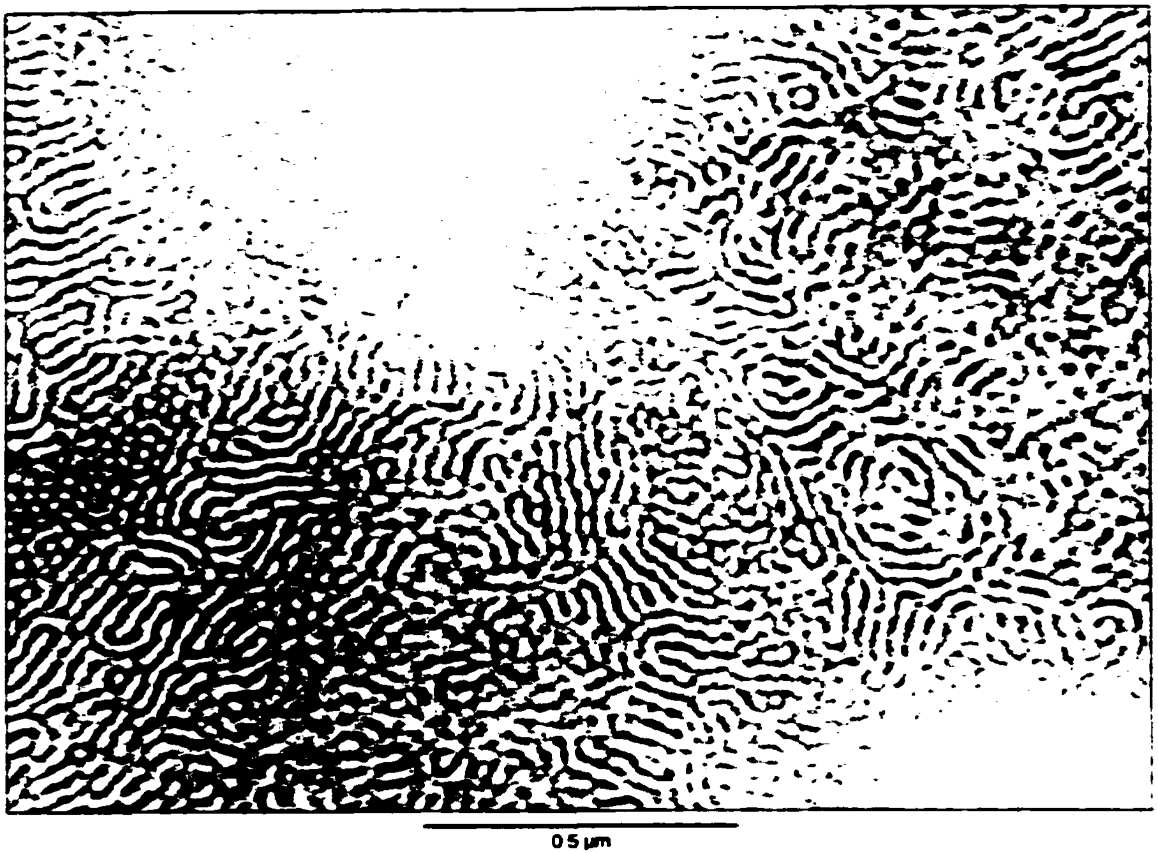
DSC of Hydrogenated Poly(PMB).



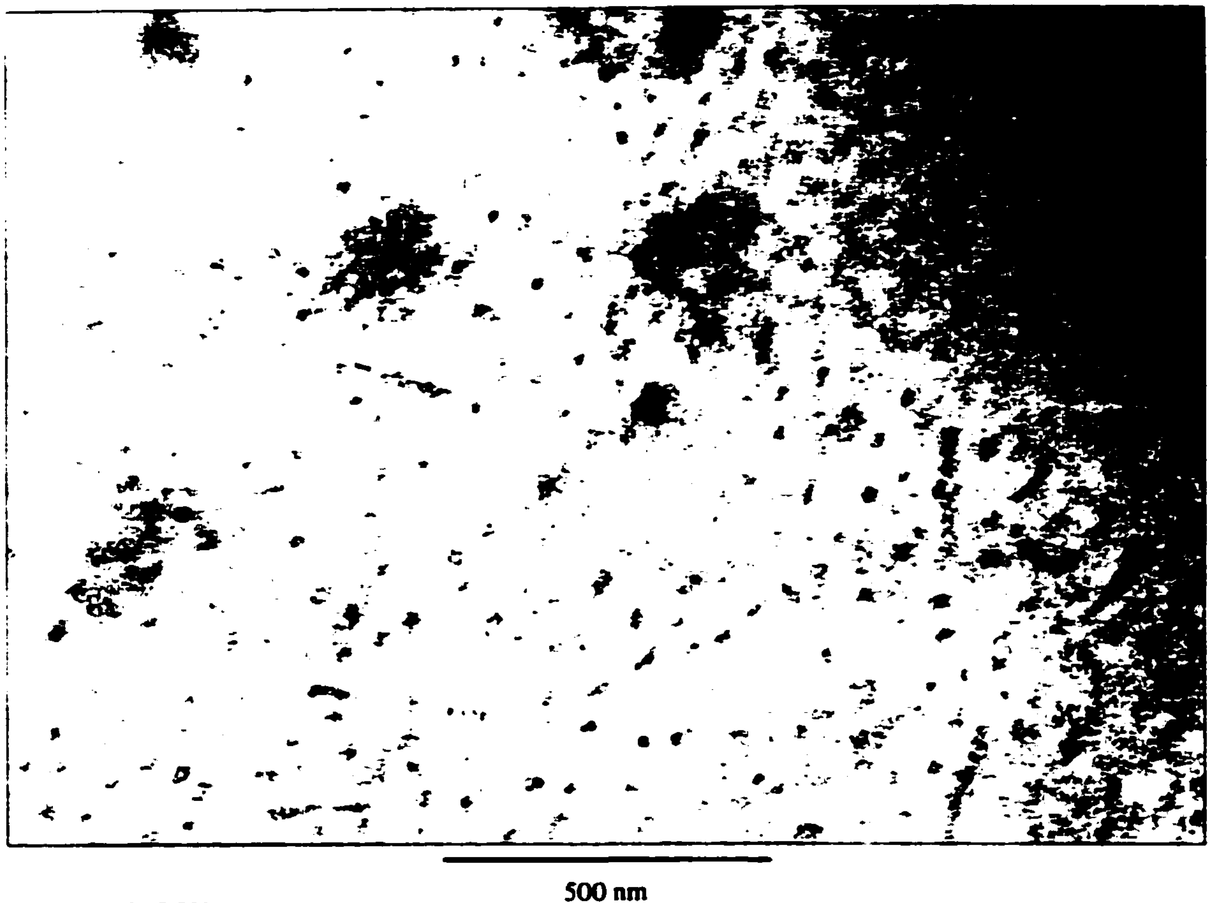
TEM of 5-31A, 75K, 13



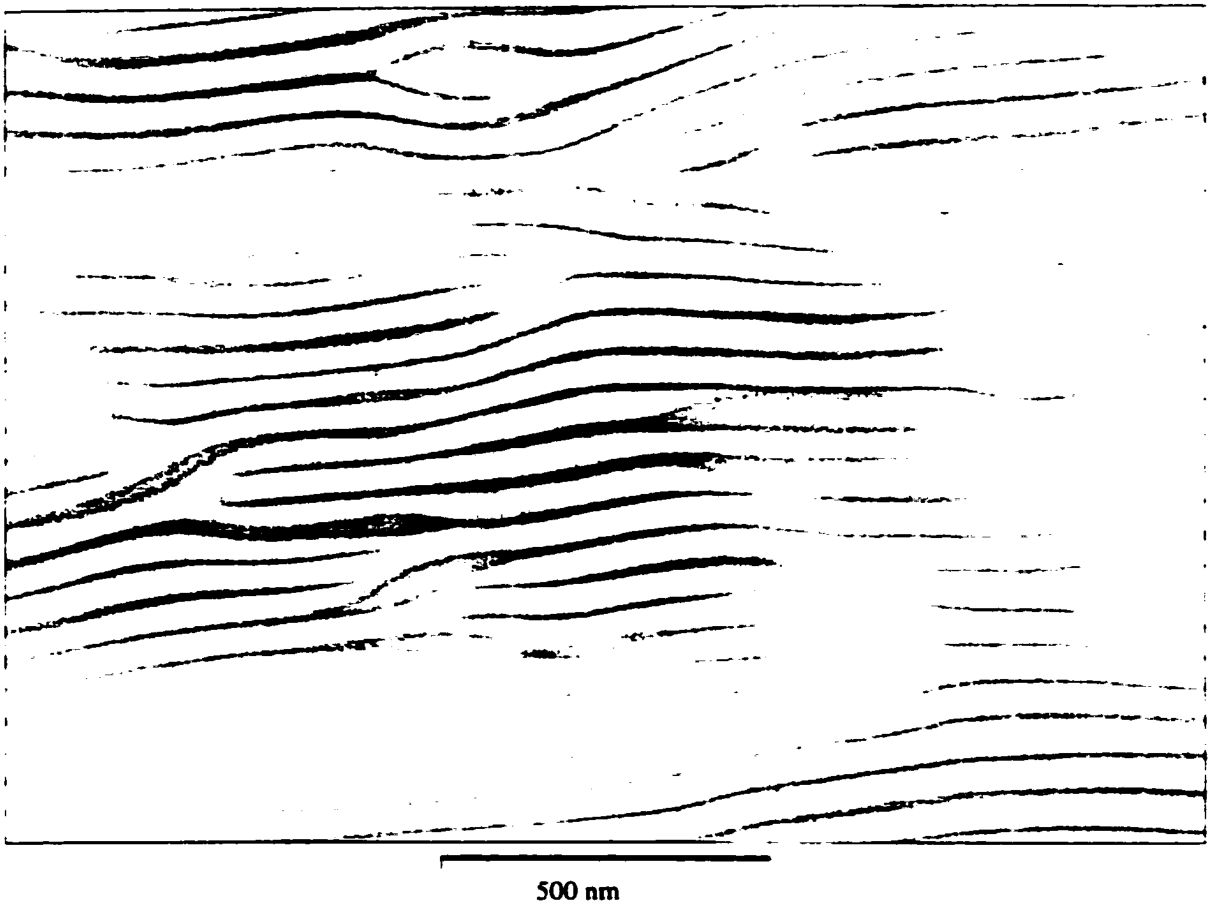
TEM of 5-31B, 75K, 14



TEM of 5-31C. 75K. **15**

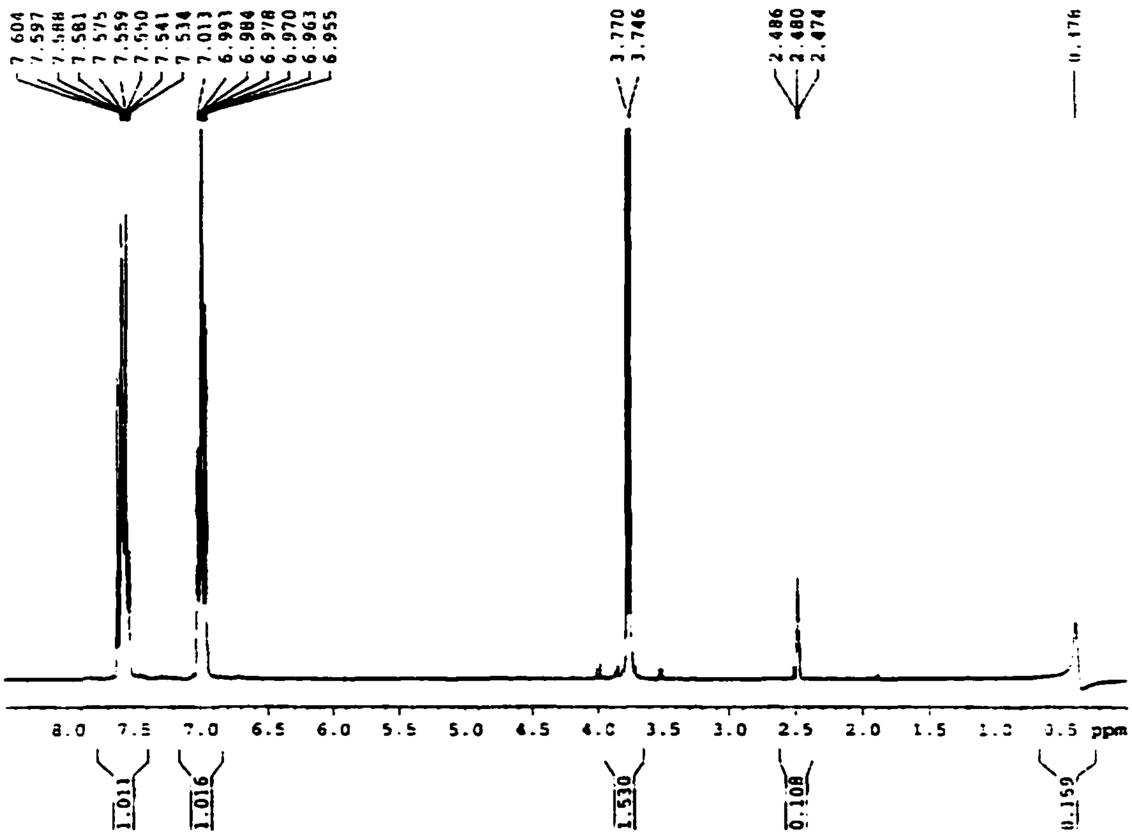


TEM of 9. 75K.

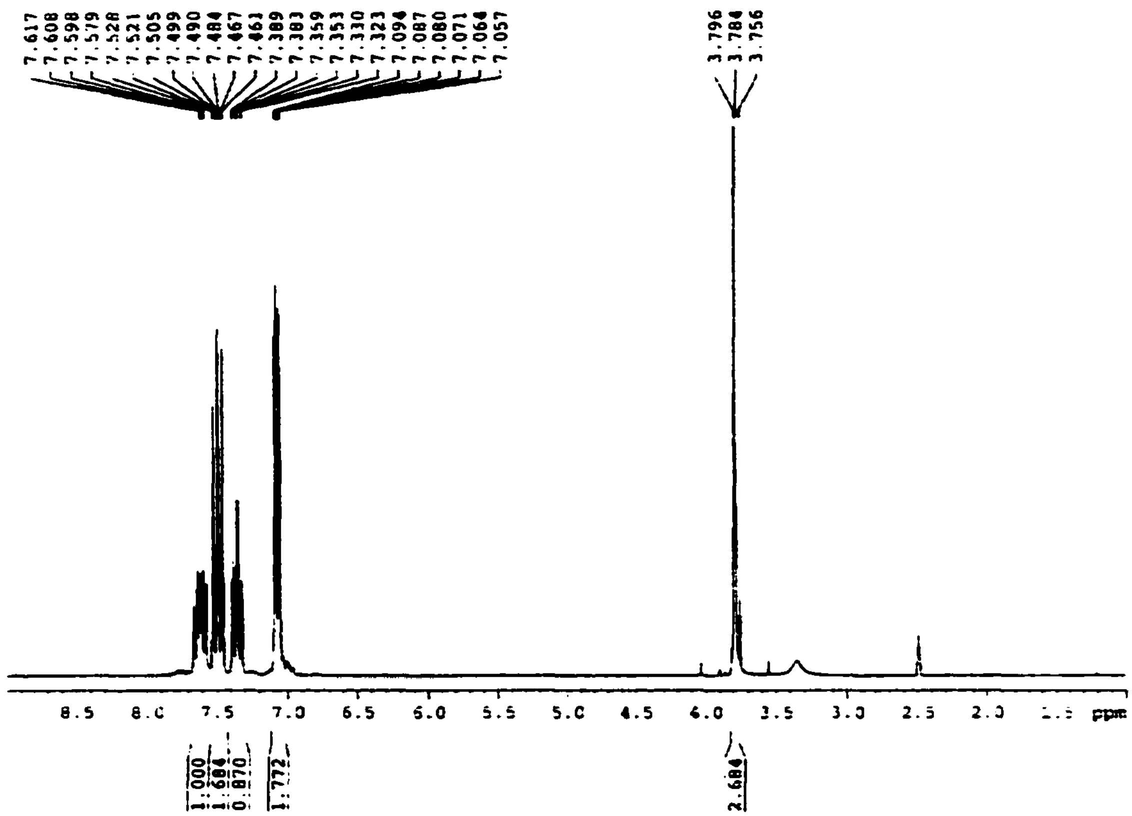


TEM of **9** after quaternization. 75K.

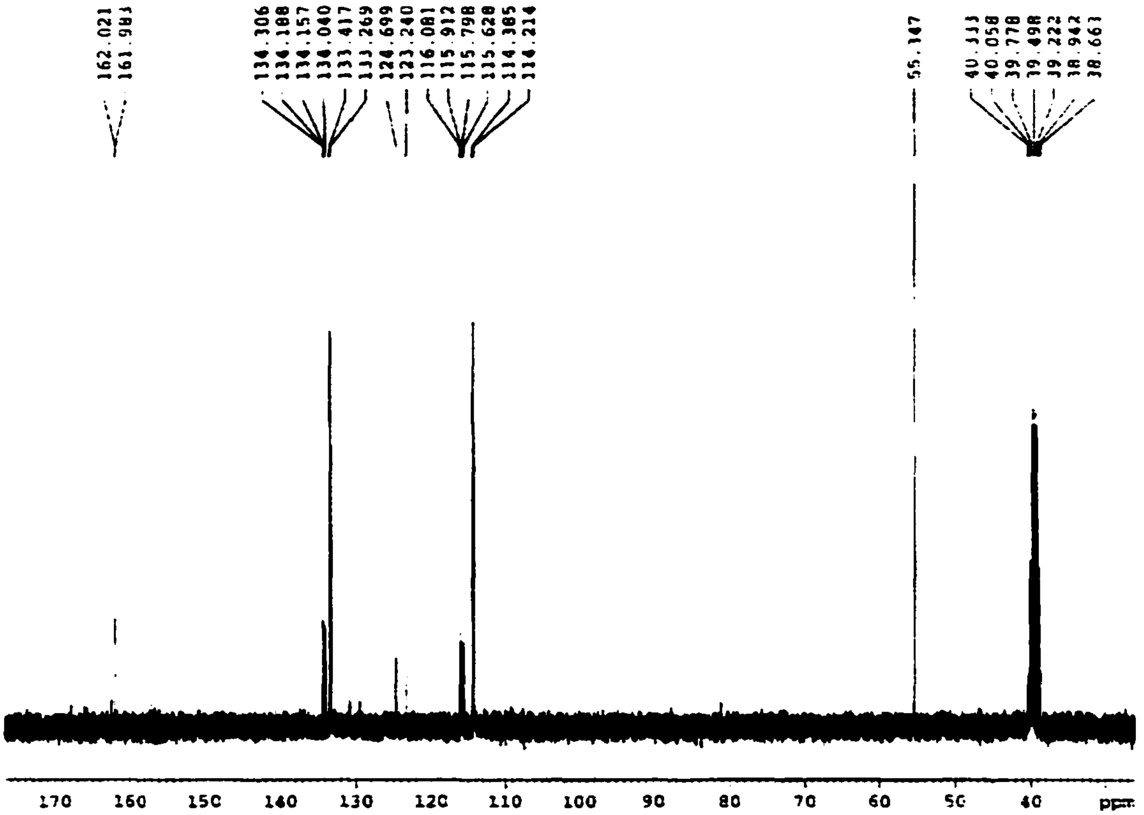
APPENDIX C. SUPPEMENTAL DATA FOR CHAPTER 4



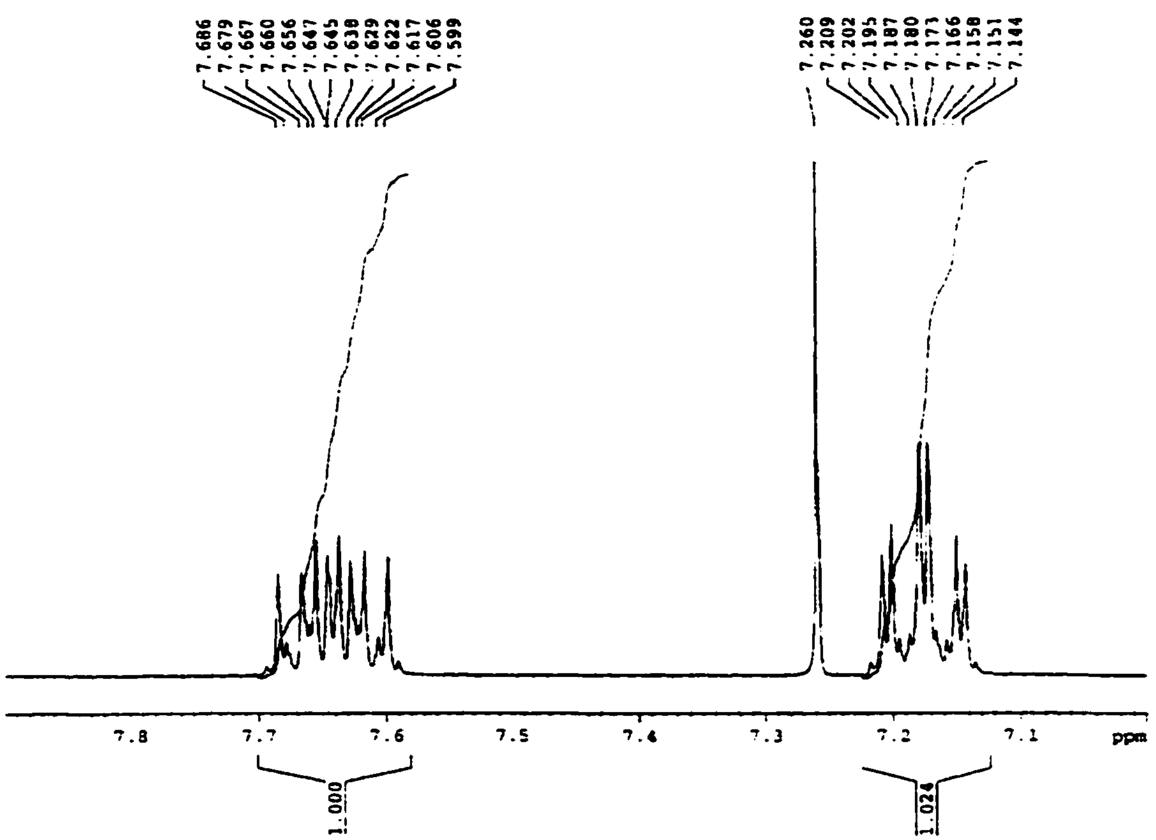
^{1}H NMR of Bis(4-methoxyphenyl)phosphinic chloride.



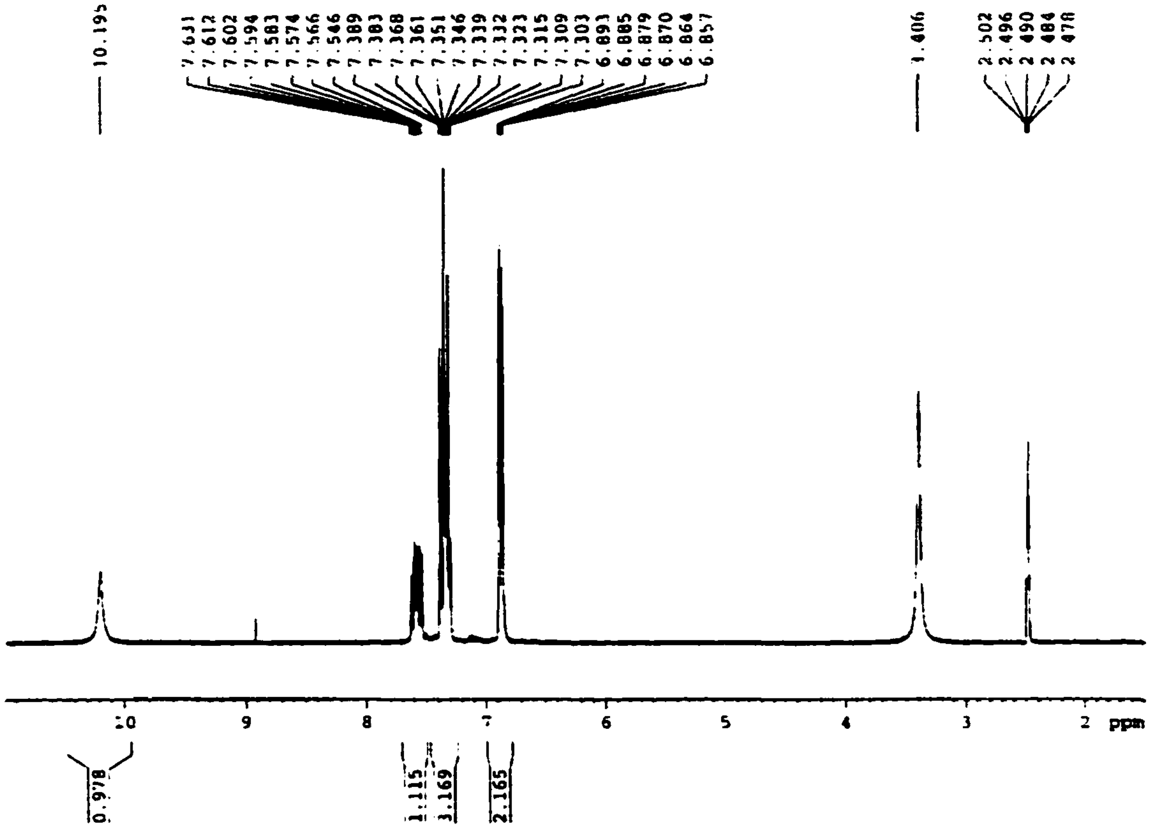
^{1}H NMR of 4-(fluorphenyl)-4',4''-(bismethoxyphenyl)phosphine oxide.



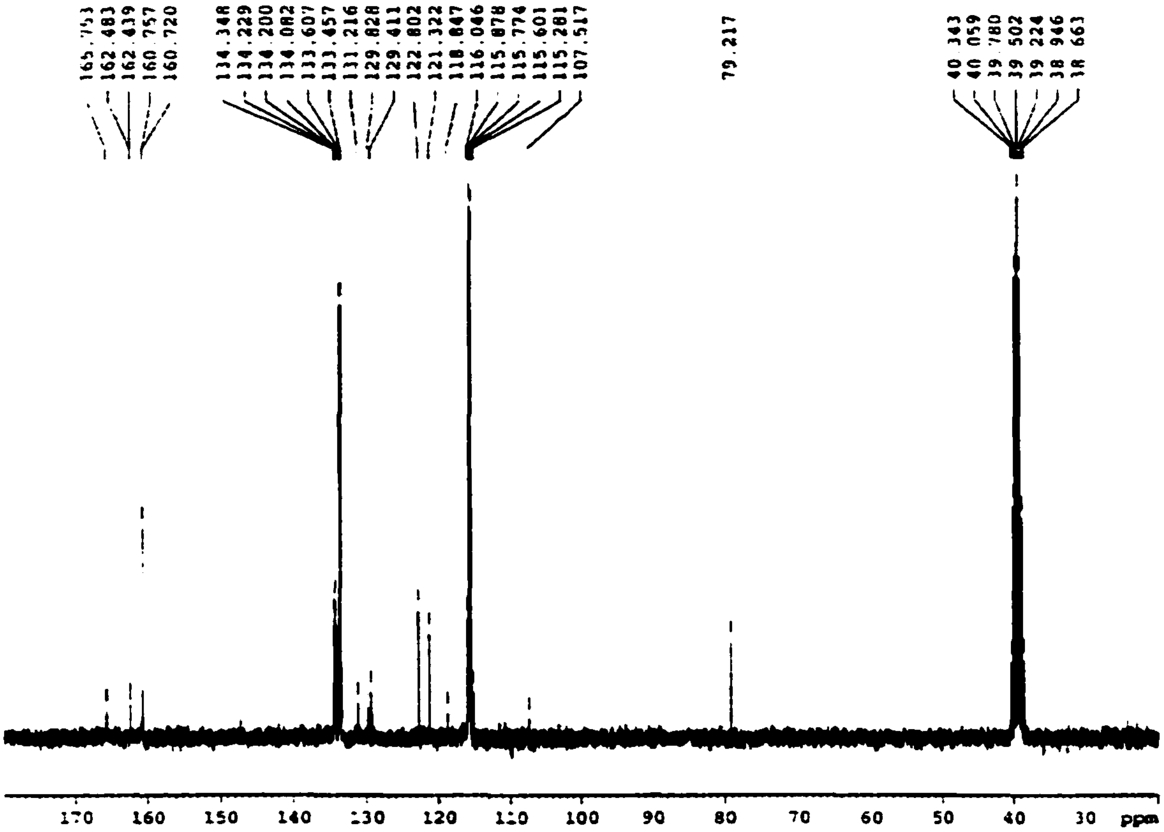
^{13}C NMR of 4-(fluorphenyl)-4',4"-(bismethoxyphenyl)phosphine oxide.



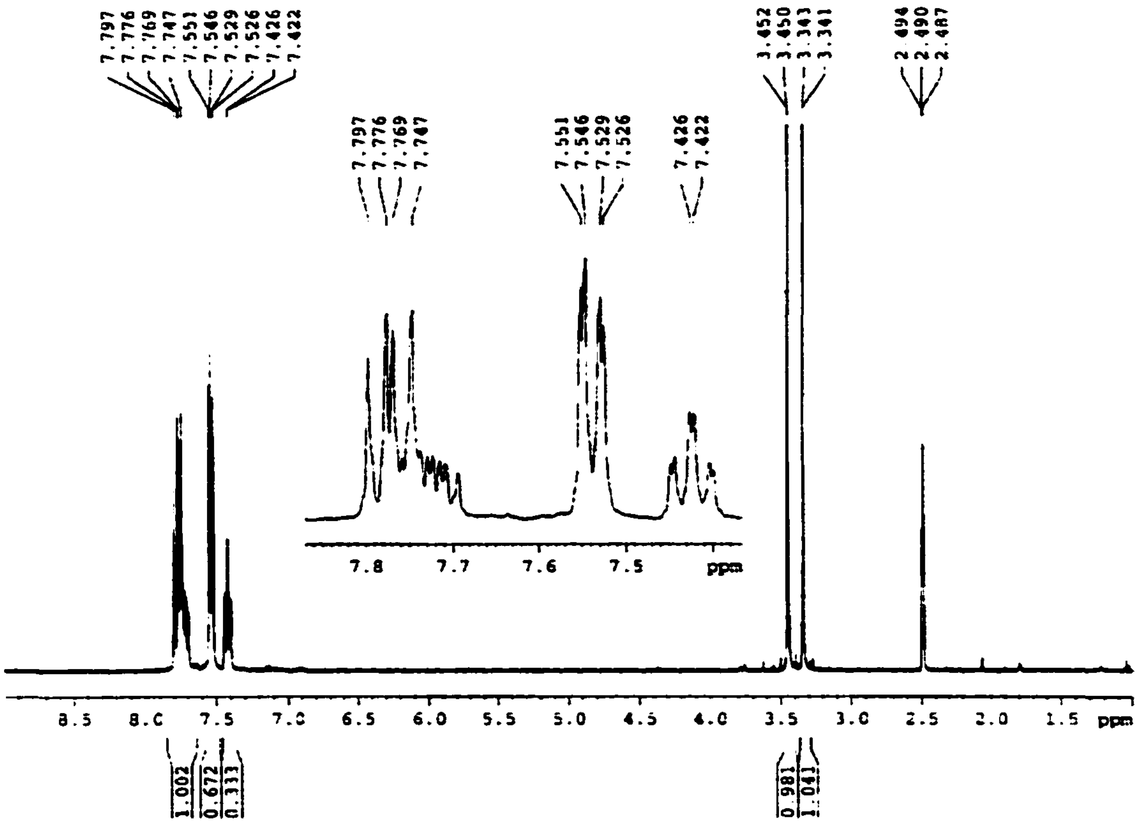
^{1}H NMR of 4.4',4''-tri(fluorophenyl)phosphine oxide.



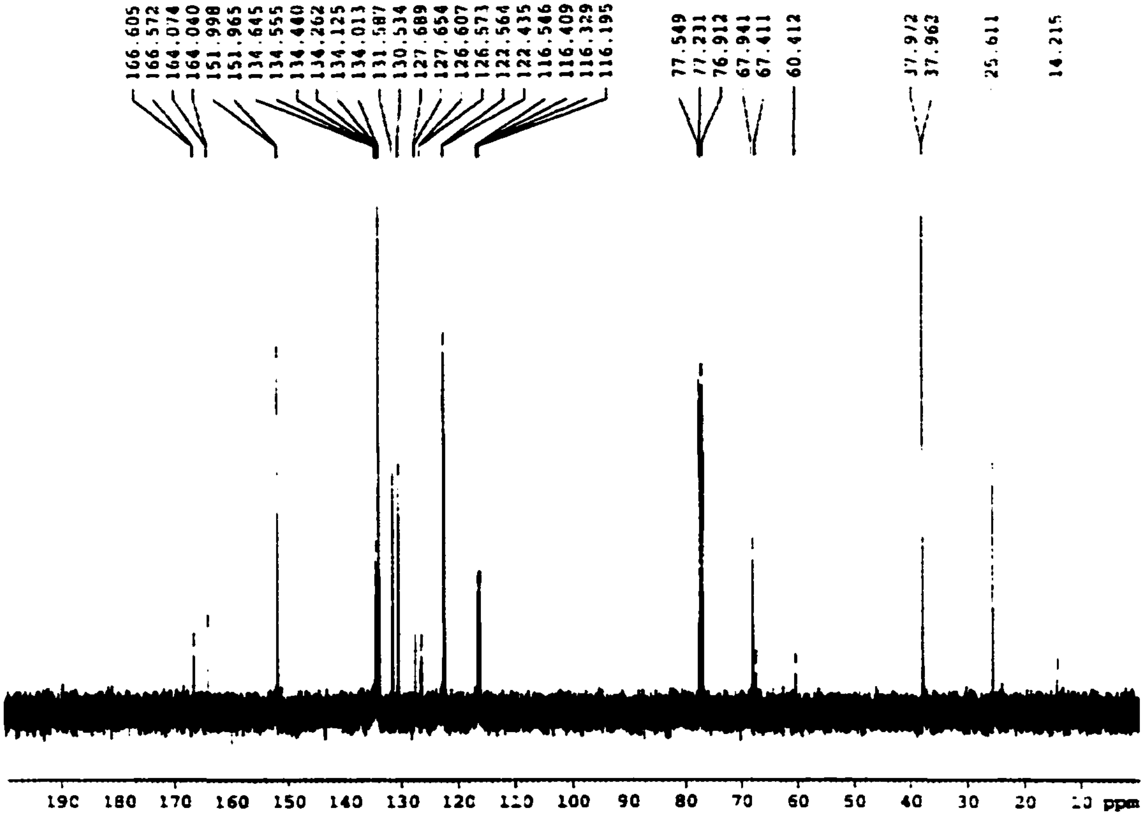
^{1}H NMR of 4-(fluorophenyl)-4',4"-(bishydroxyphenyl)phosphine oxide (1).



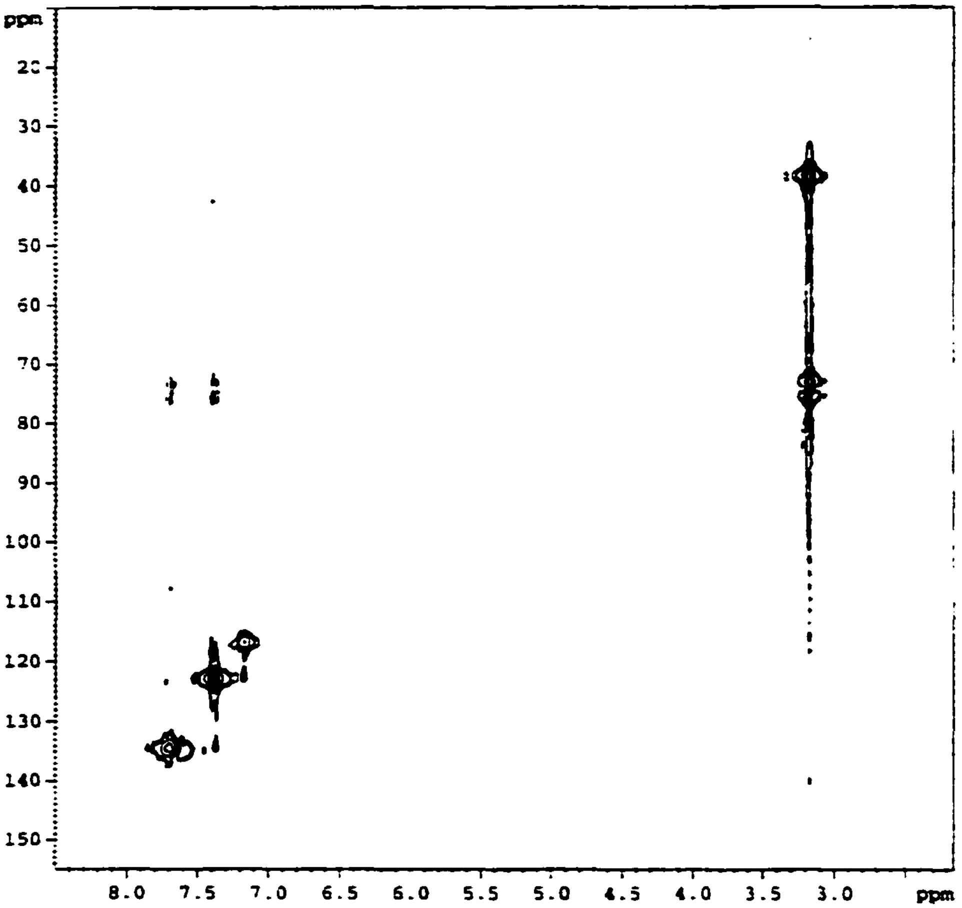
^{13}C NMR of 4-(fluorophenyl)-4',4''-(bishydroxyphenyl)phosphine oxide (1).



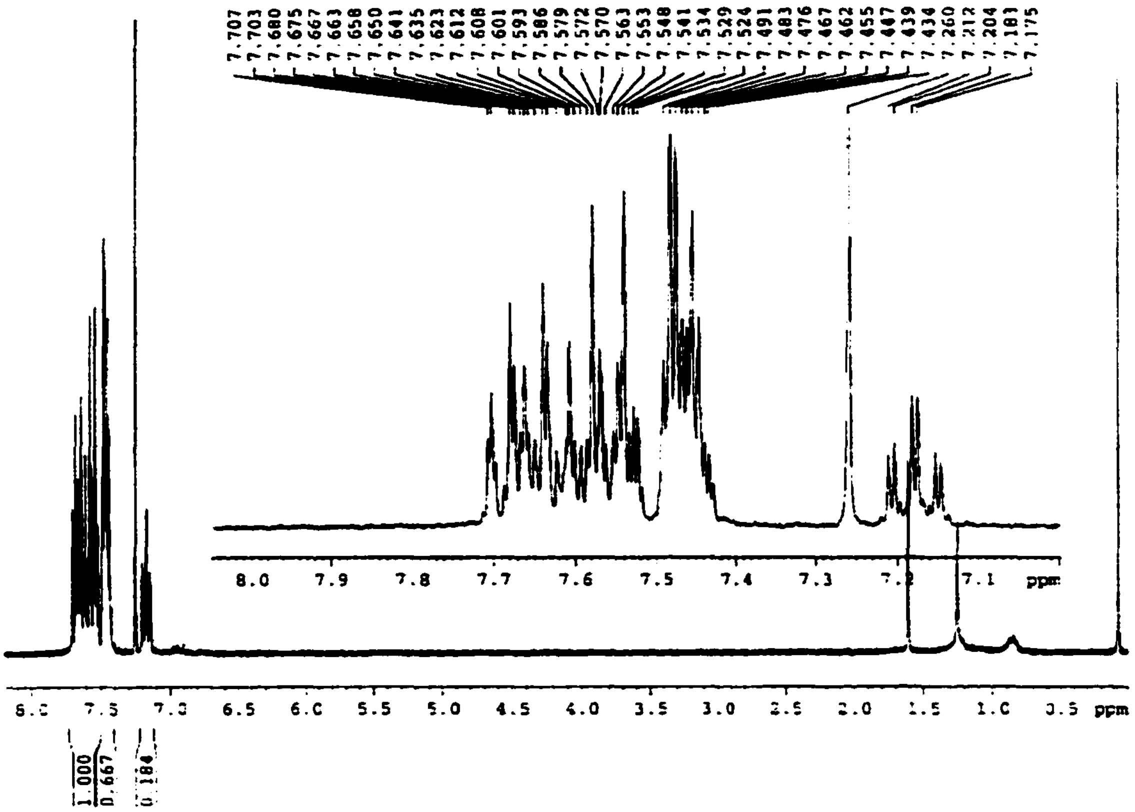
^{1}H NMR of 4-(Fluorophenyl)-4',4''-di(methanesulfonyloxyphenyl)phosphine oxide (2).



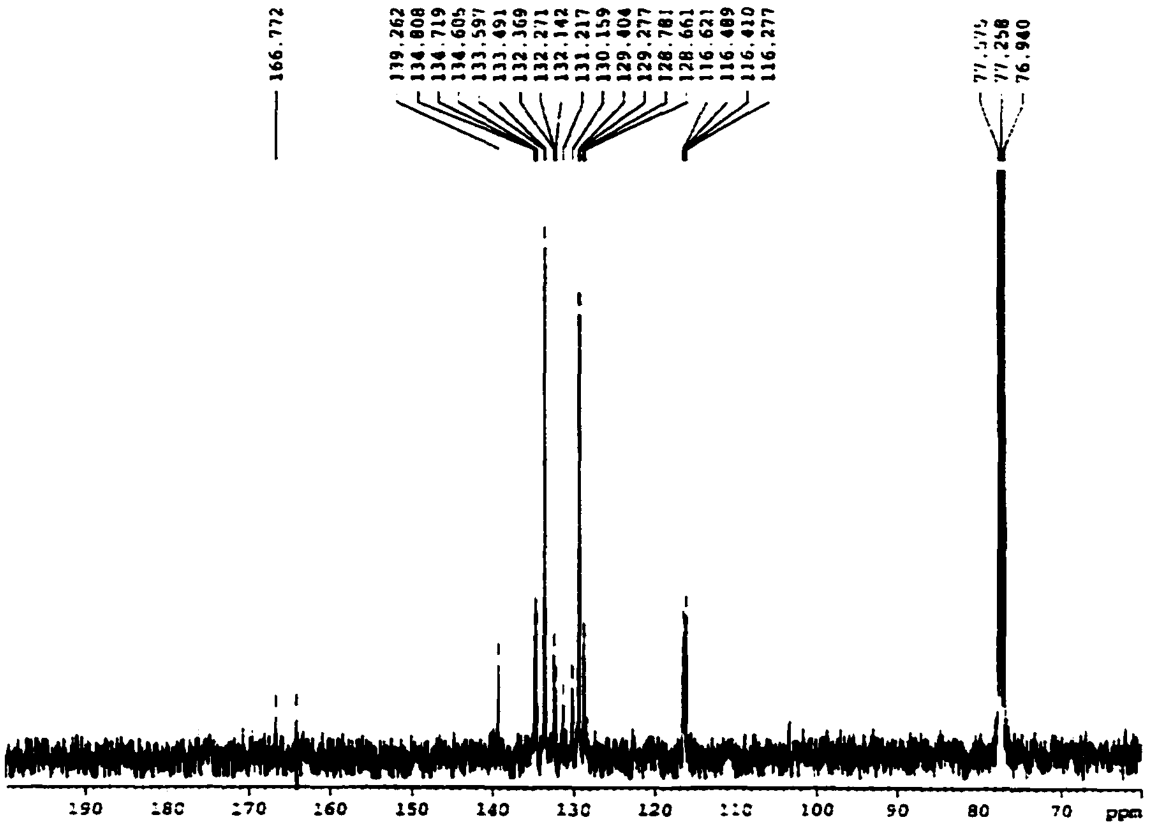
^{13}C NMR of 4-(Fluorophenyl)-4',4''-di(methanesulfonyloxyphenyl)phosphine oxide (2).



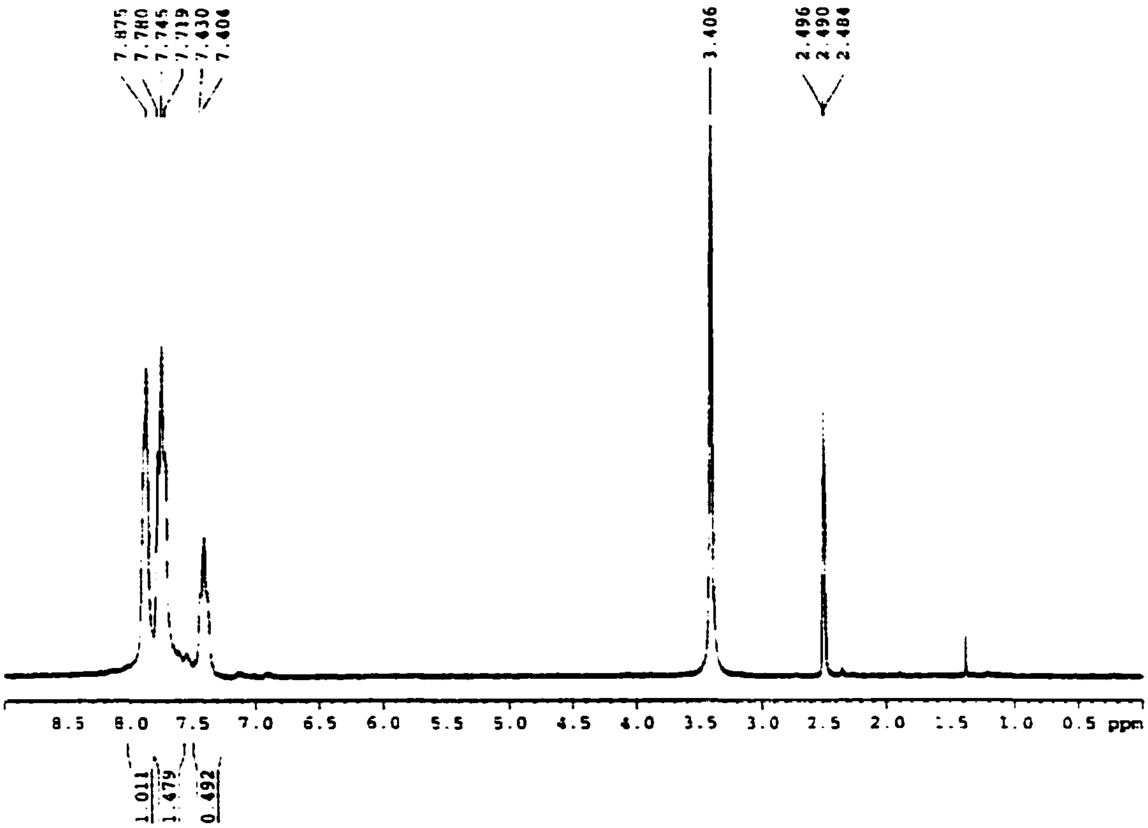
NOESY of 4-(Fluorophenyl)-4',4''-di(methanesulfonyloxyphenyl)phosphine oxide (2).



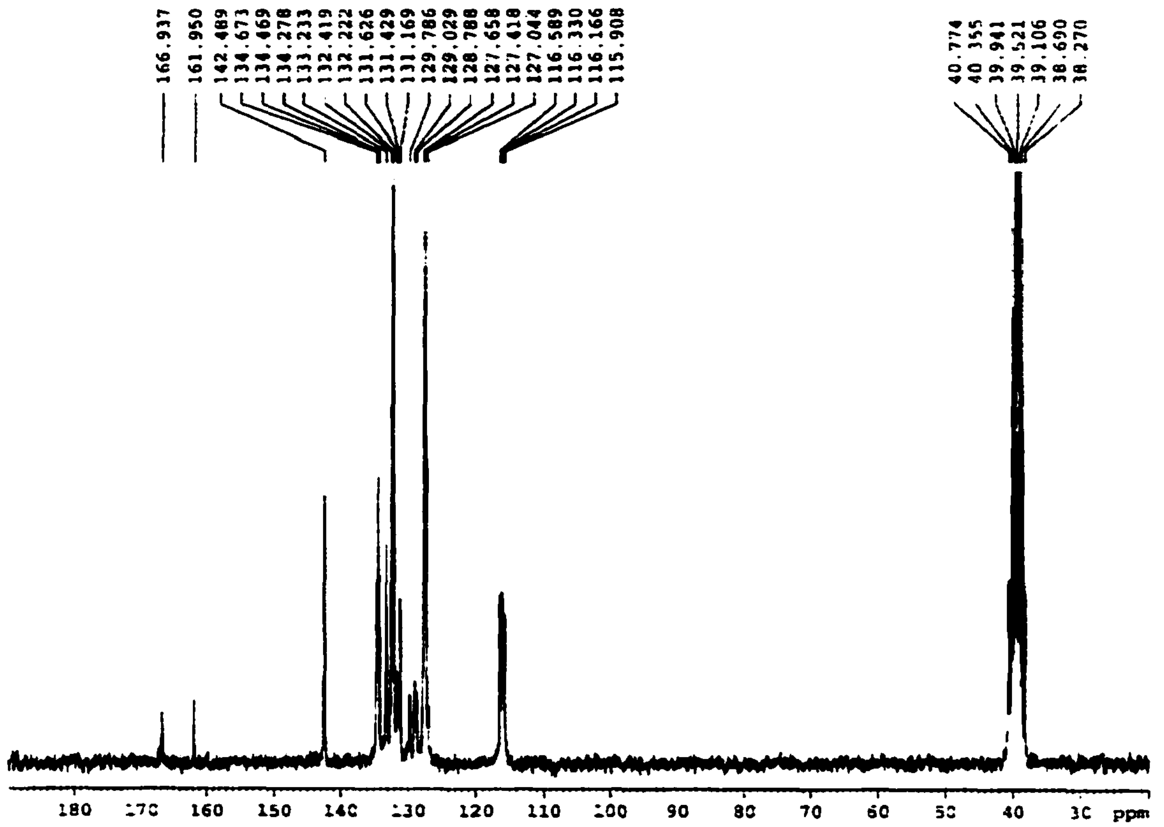
^{1}H NMR of 4-(Fluorophenyl)-4',4''-di(chlorophenyl)phosphine oxide (3).



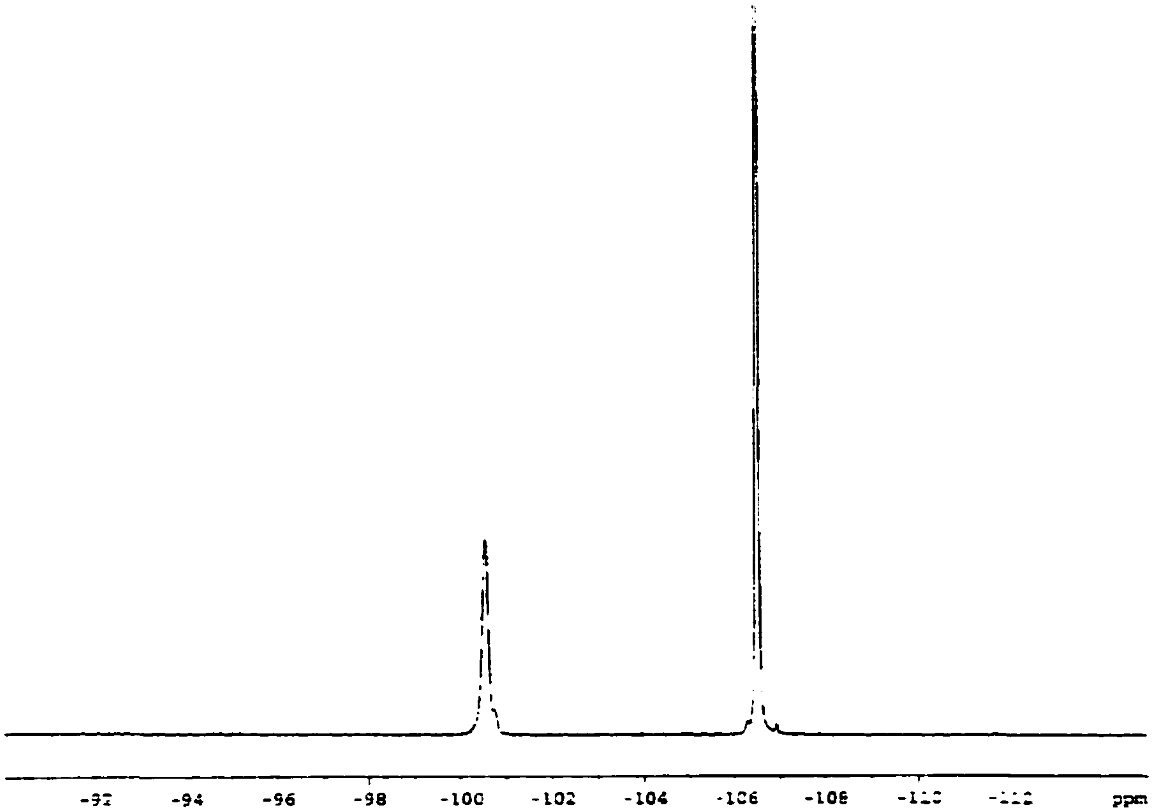
^{13}C NMR of 4-(Fluorophenyl)-4',4''-di(chlorophenyl)phosphine oxide (3).



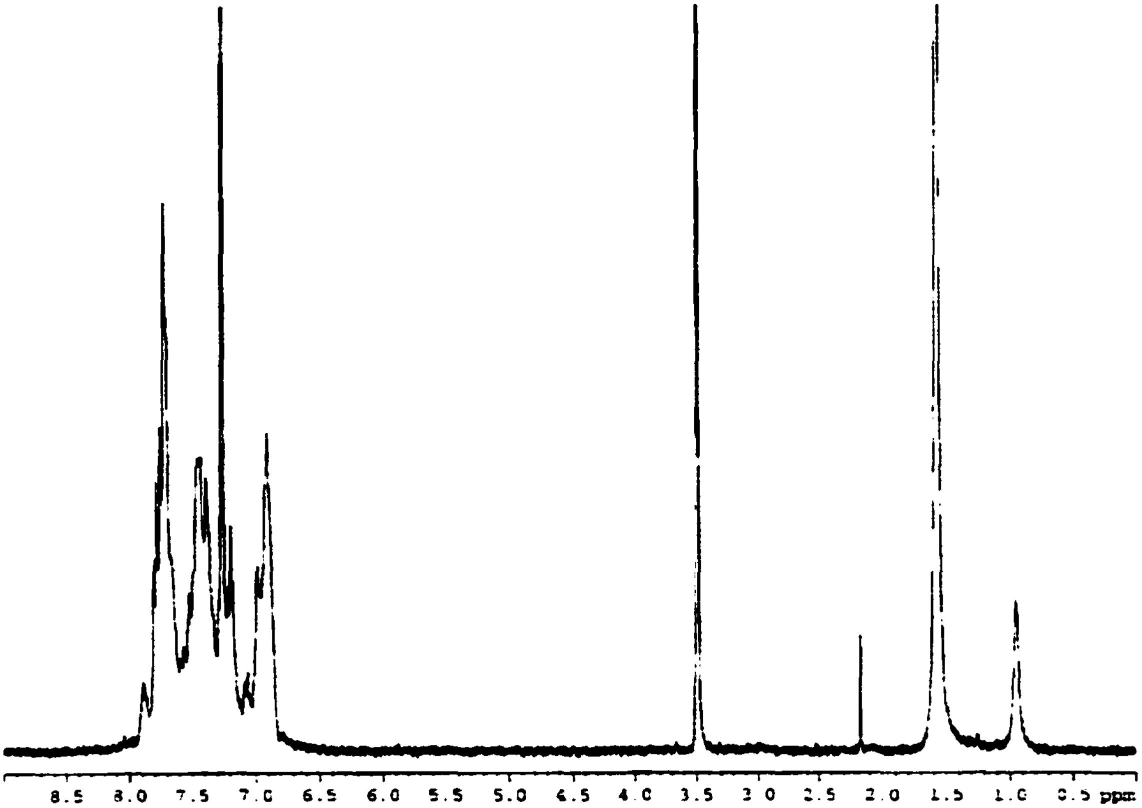
^{1}H NMR of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (4. 5).



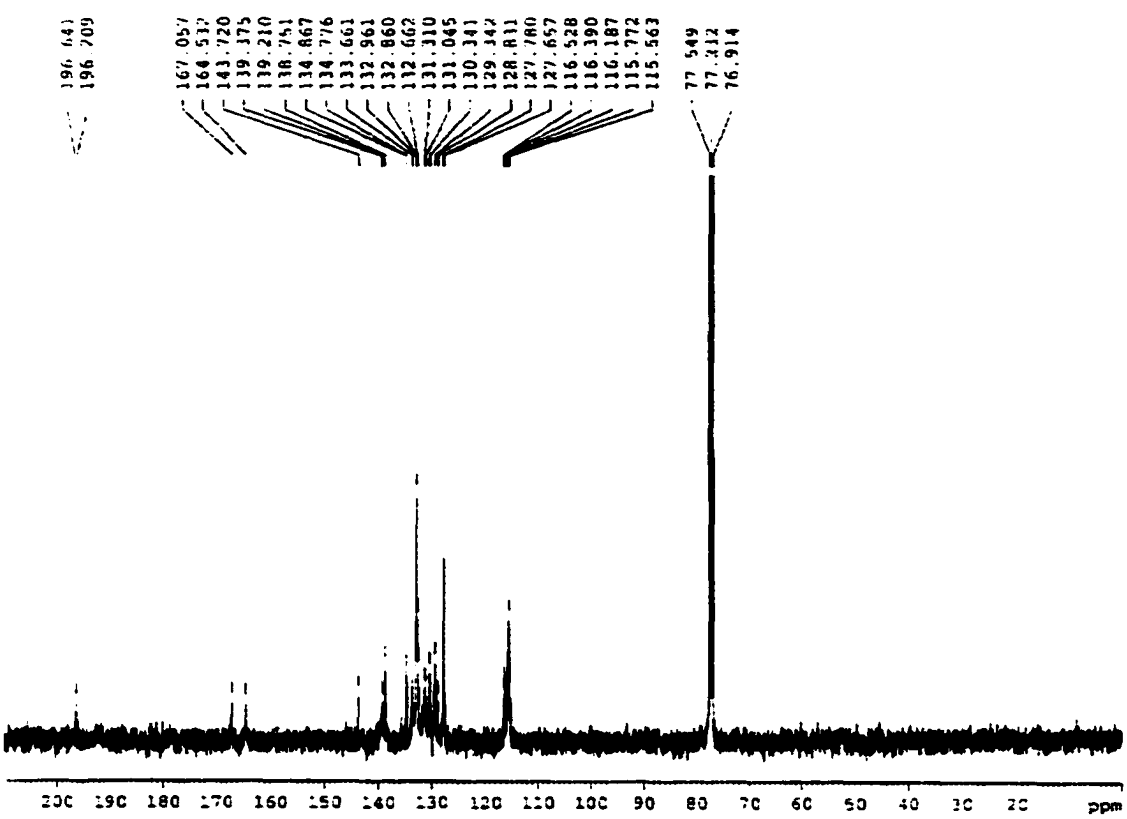
^{13}C NMR of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (4. 5).



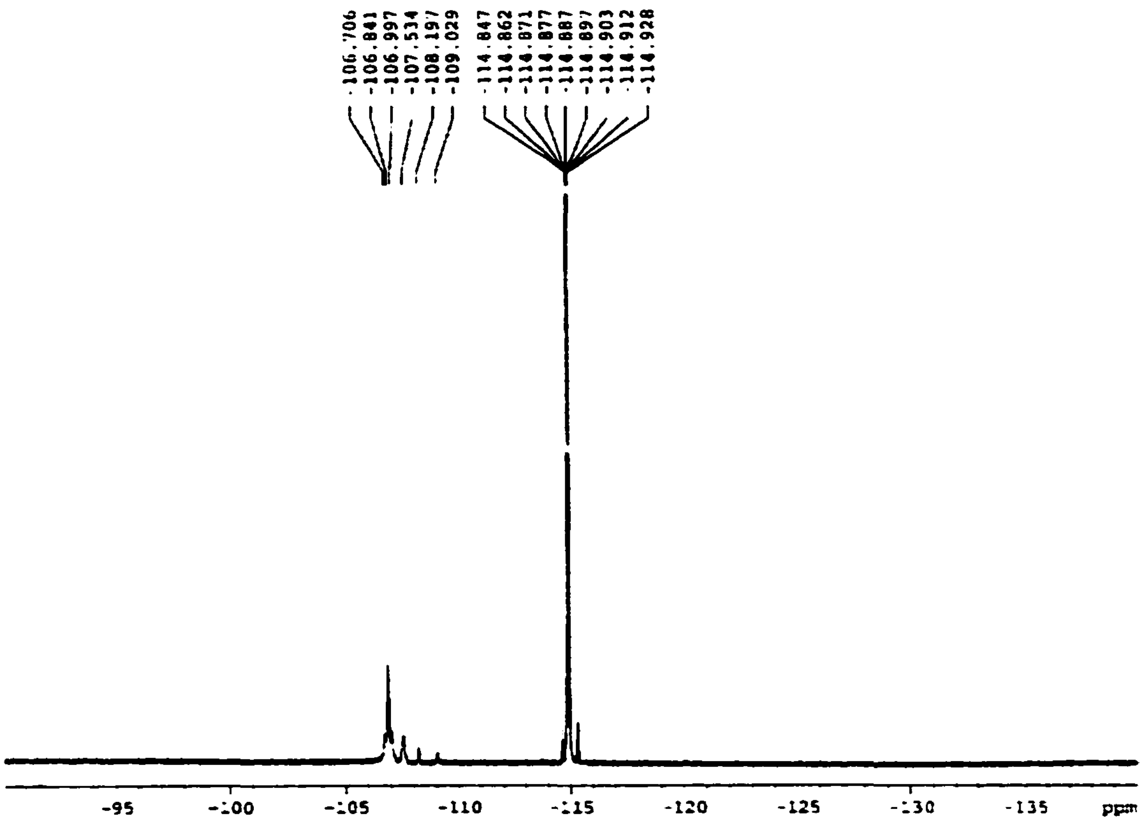
^{19}F of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (5).



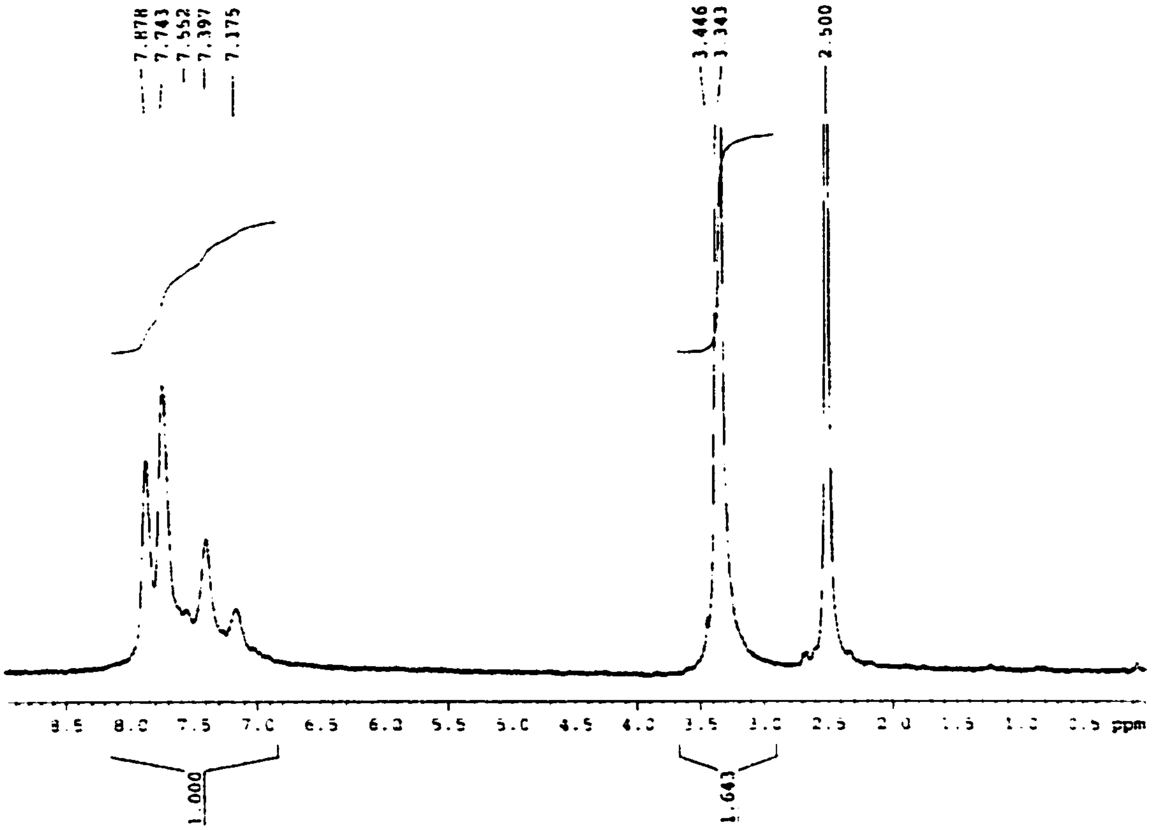
^{1}H NMR of PAPO-*co*-PPP (7).



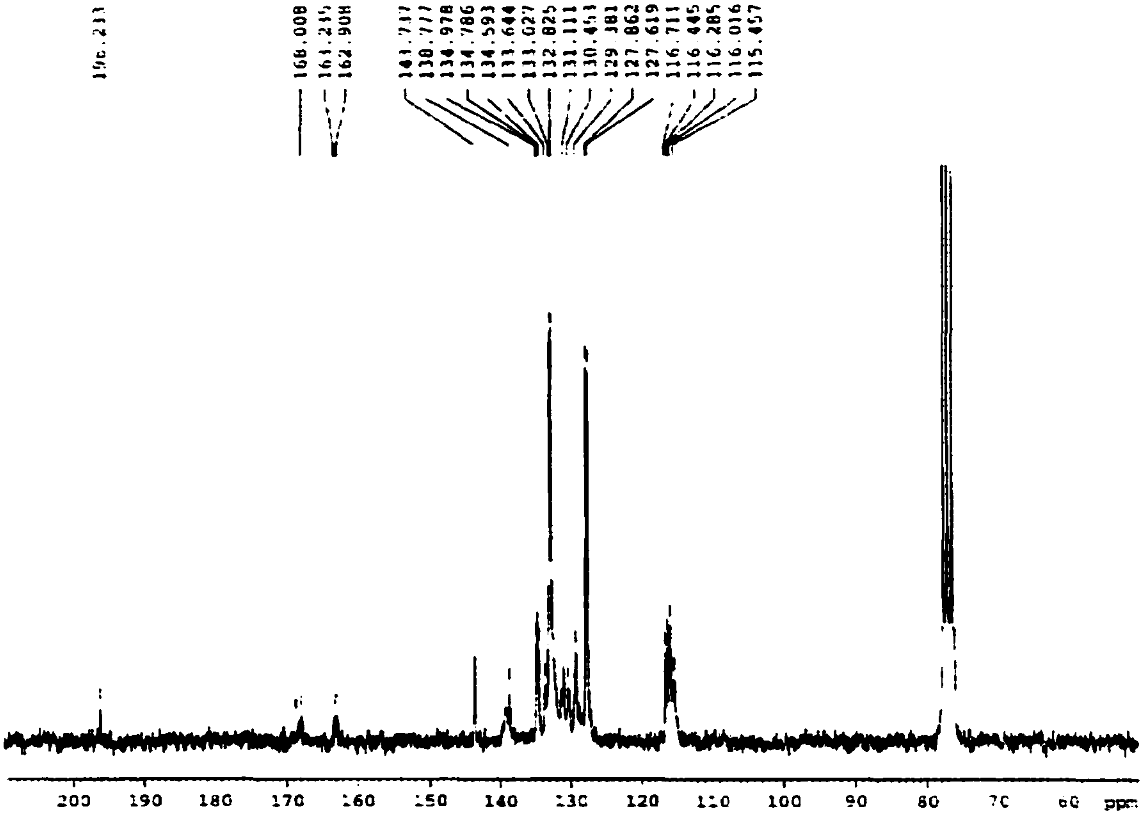
^{13}C NMR of PAPO-*co*-PPP (7).



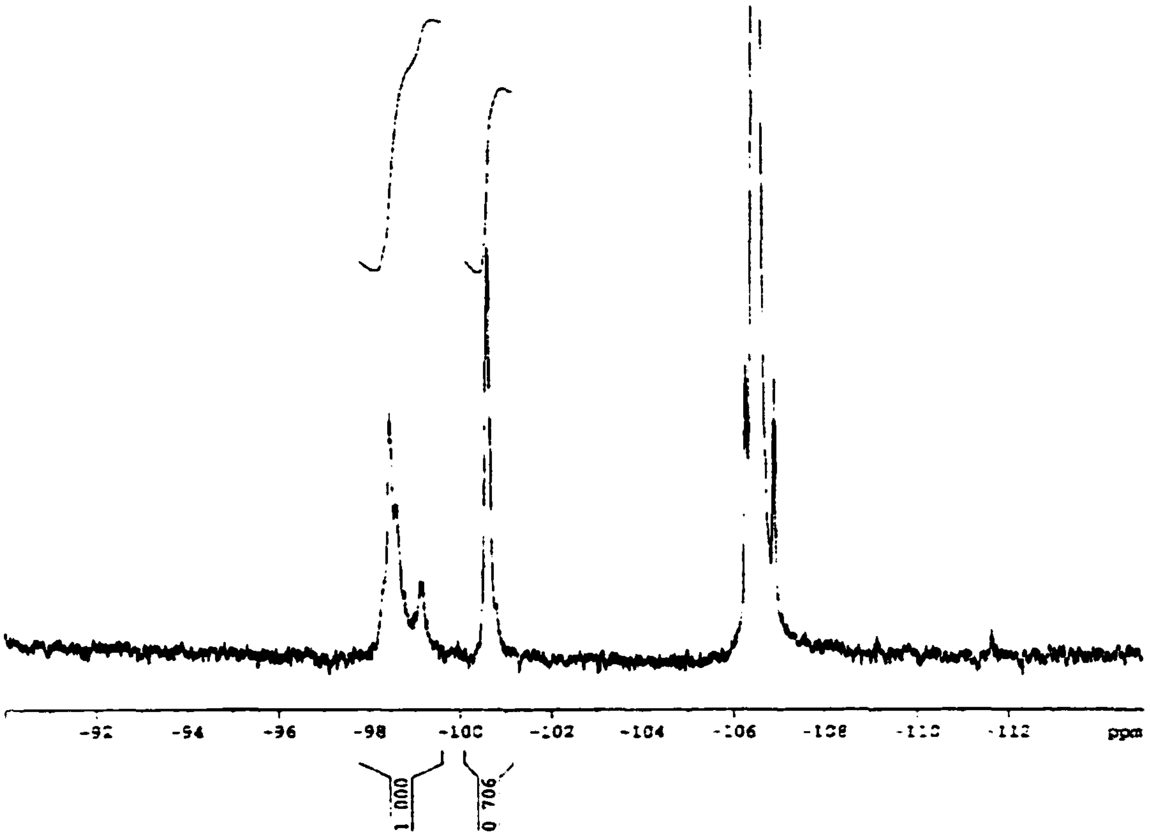
^{19}F NMR of PAPO-*co*-PPP (7).



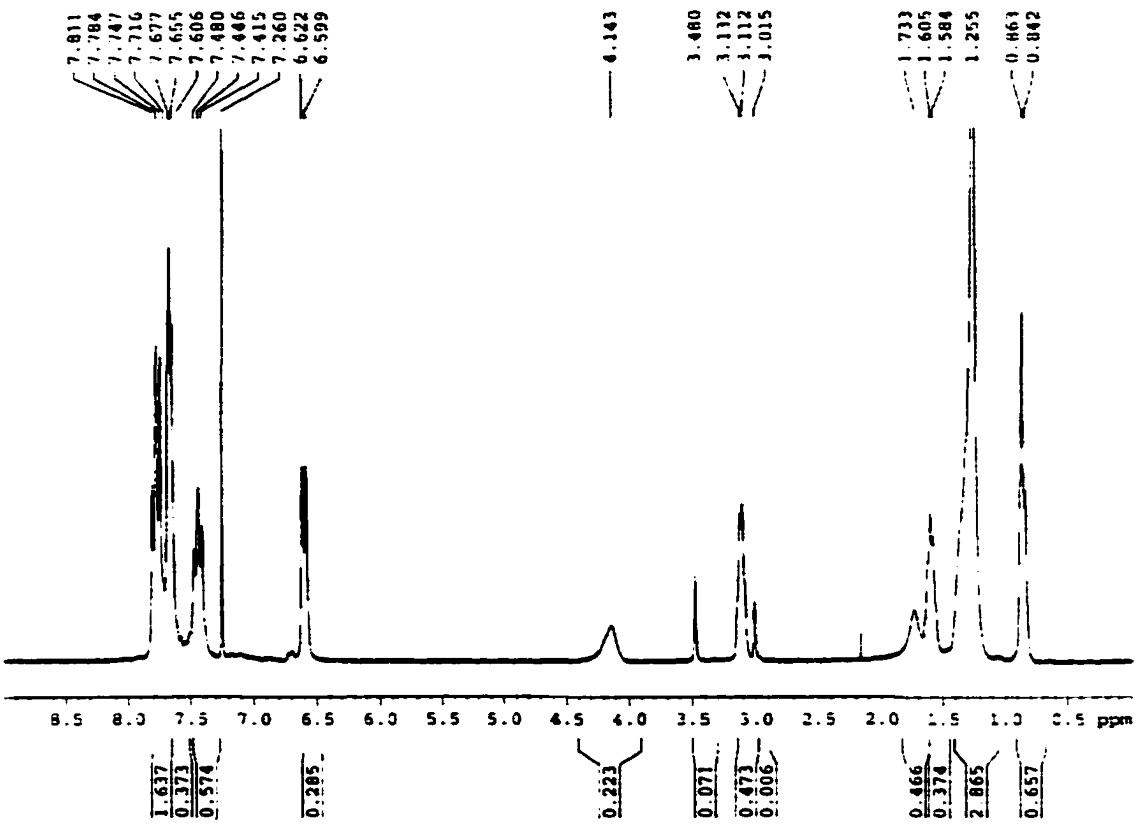
^{1}H NMR of poly(PAPO-*co*-PPP) (8).



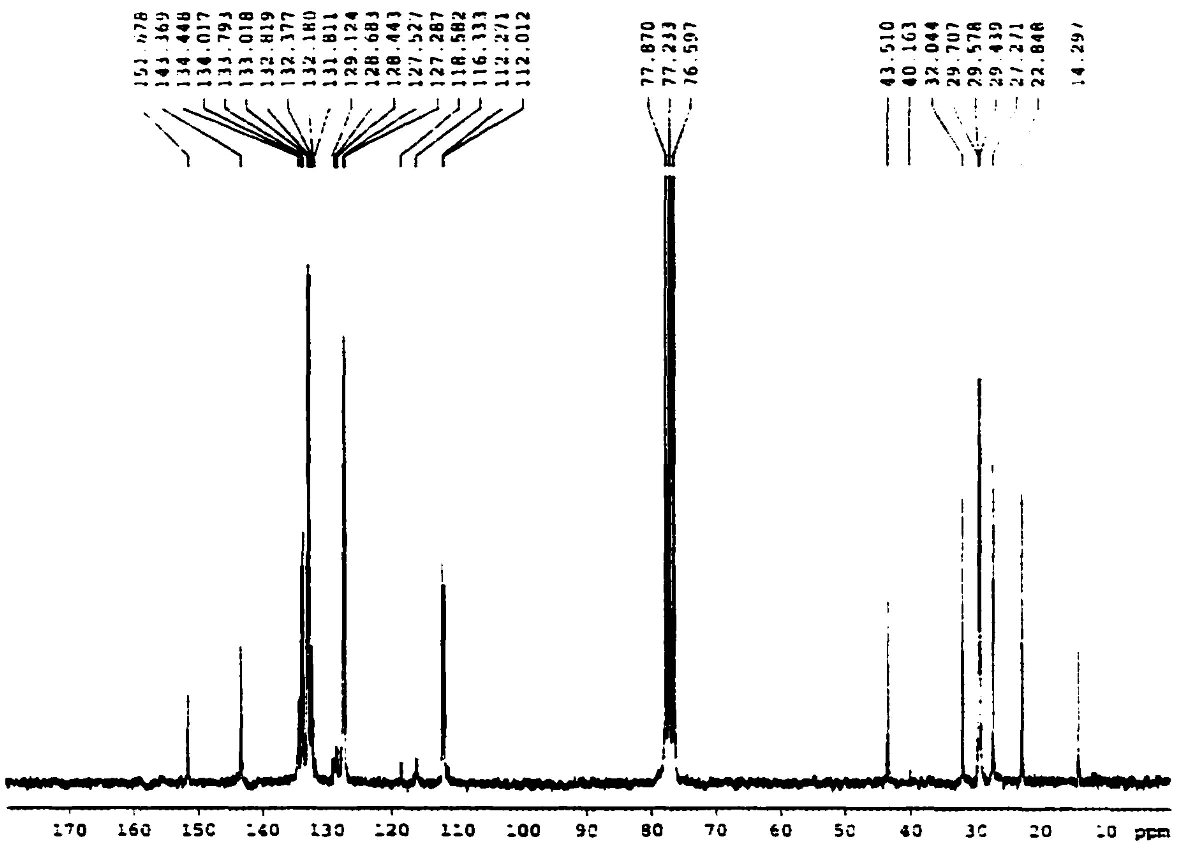
^{13}C NMR of poly(PAPO-*co*-PPP) (8).



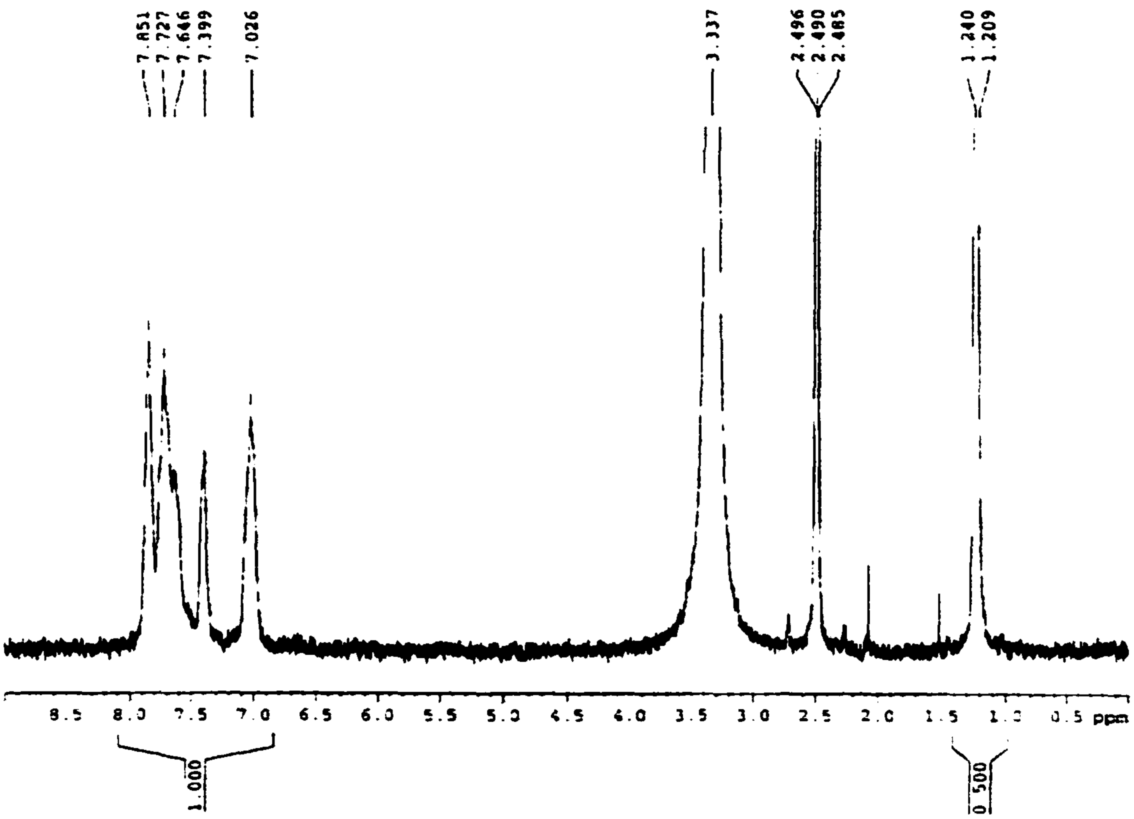
^{19}F NMR of poly(PAPO-*co*-PPP) (8).



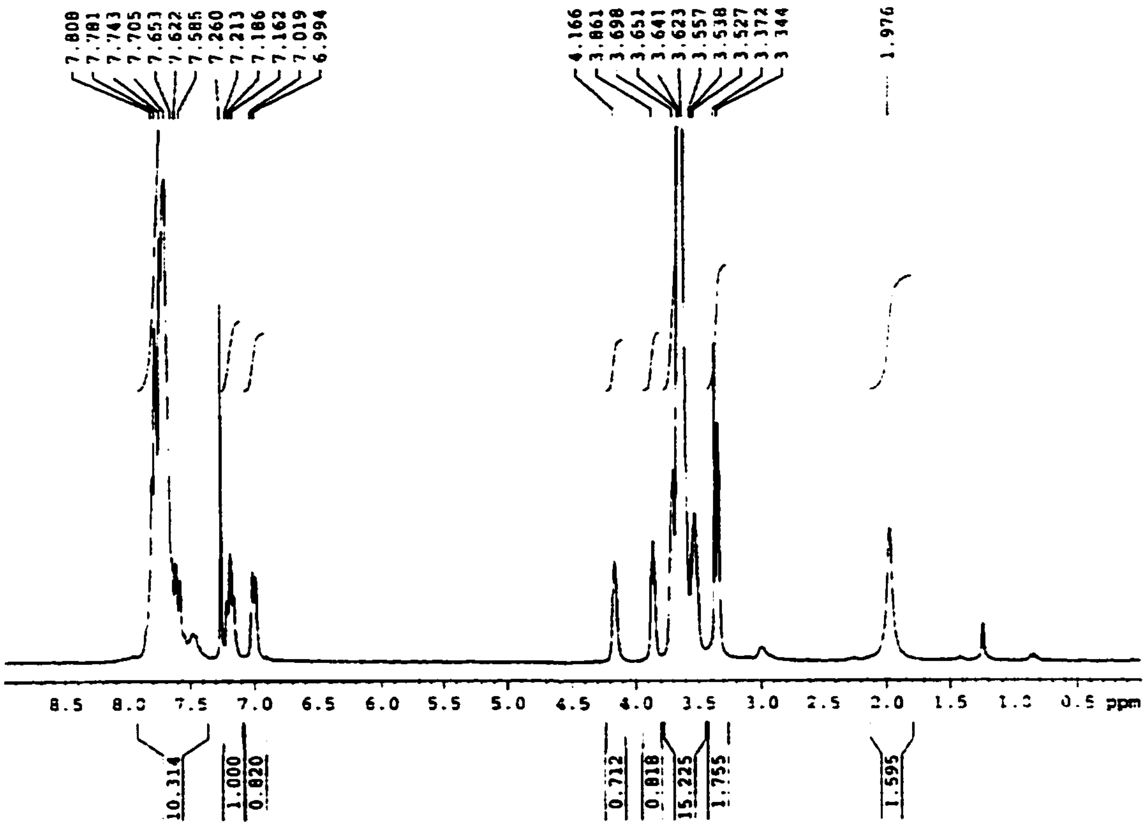
^{1}H NMR of *n*-nonylamine substituted PAPO (9).



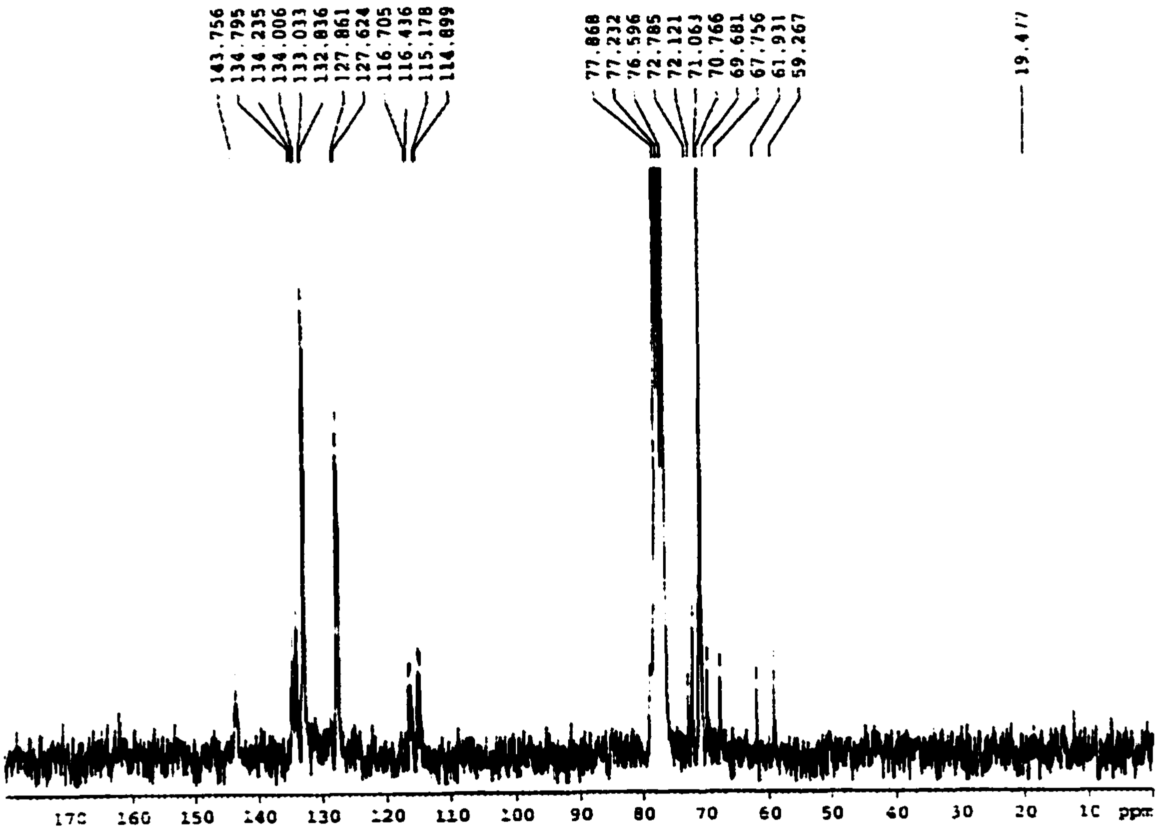
^{13}C NMR of *n*-nonylamine substituted PAPO (9).



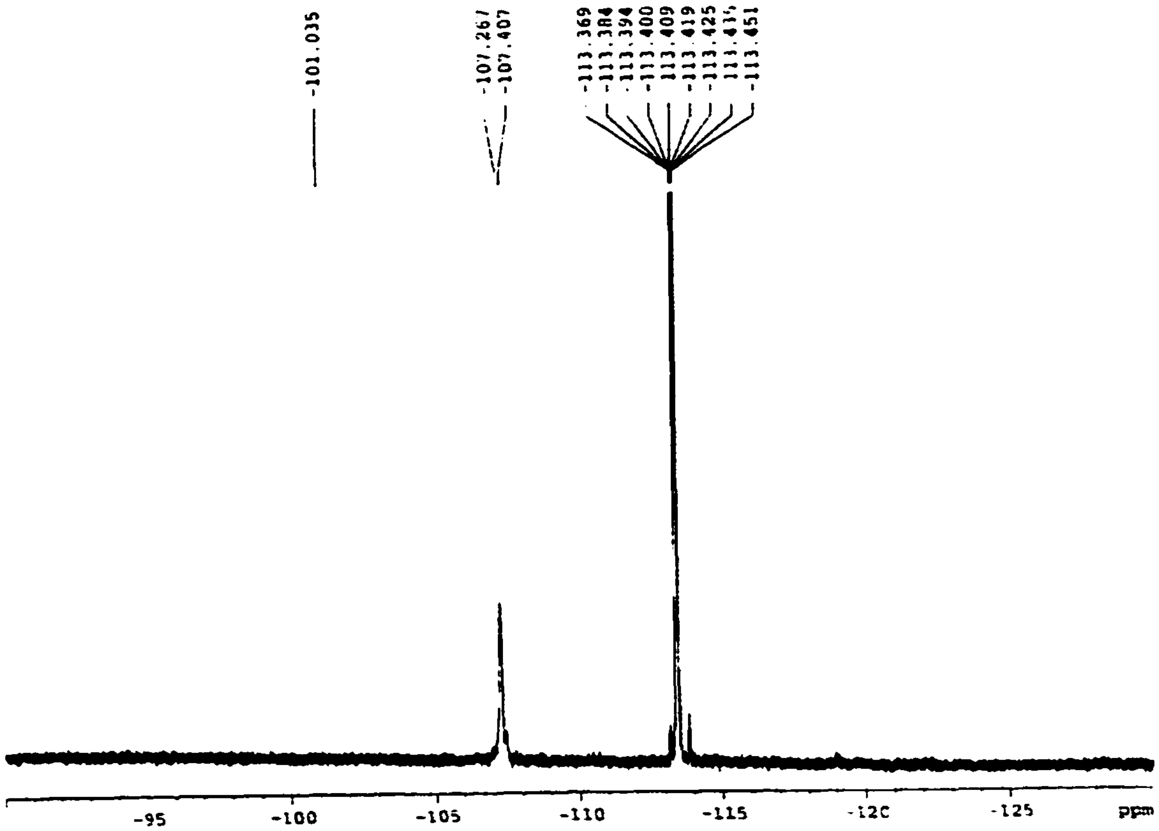
^{1}H NMR of 4-*t*-butylphenol substituted PAPO (10).



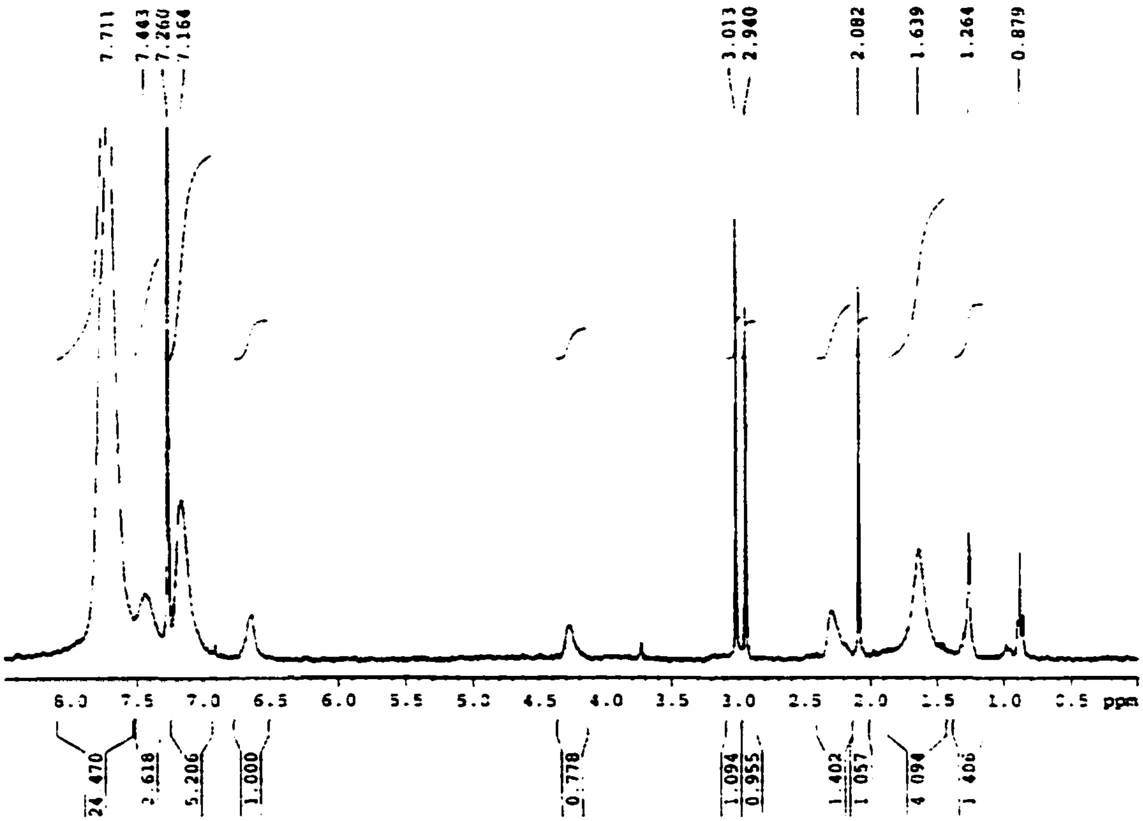
^{1}H NMR of poly(ethylene glycol)monomethylether (repeat unit average = 7) substituted PAPO (11).



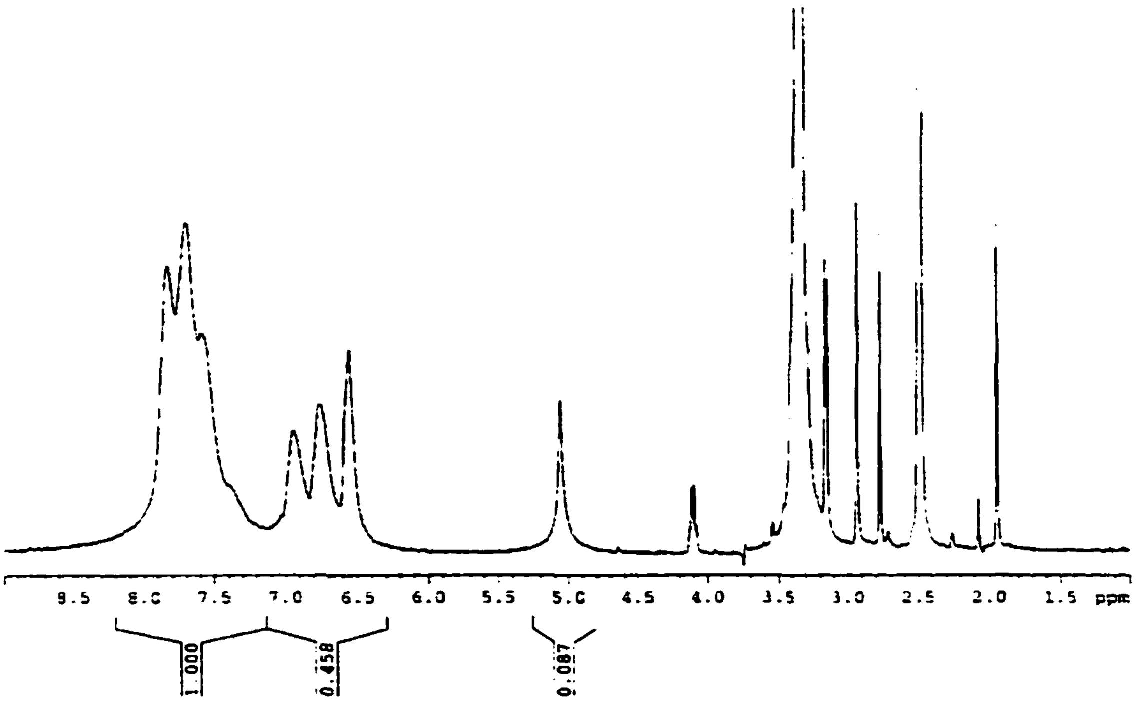
^{13}C NMR of poly(ethylene glycol)monomethylether (repeat unit average = 7) substituted PAPO (11).



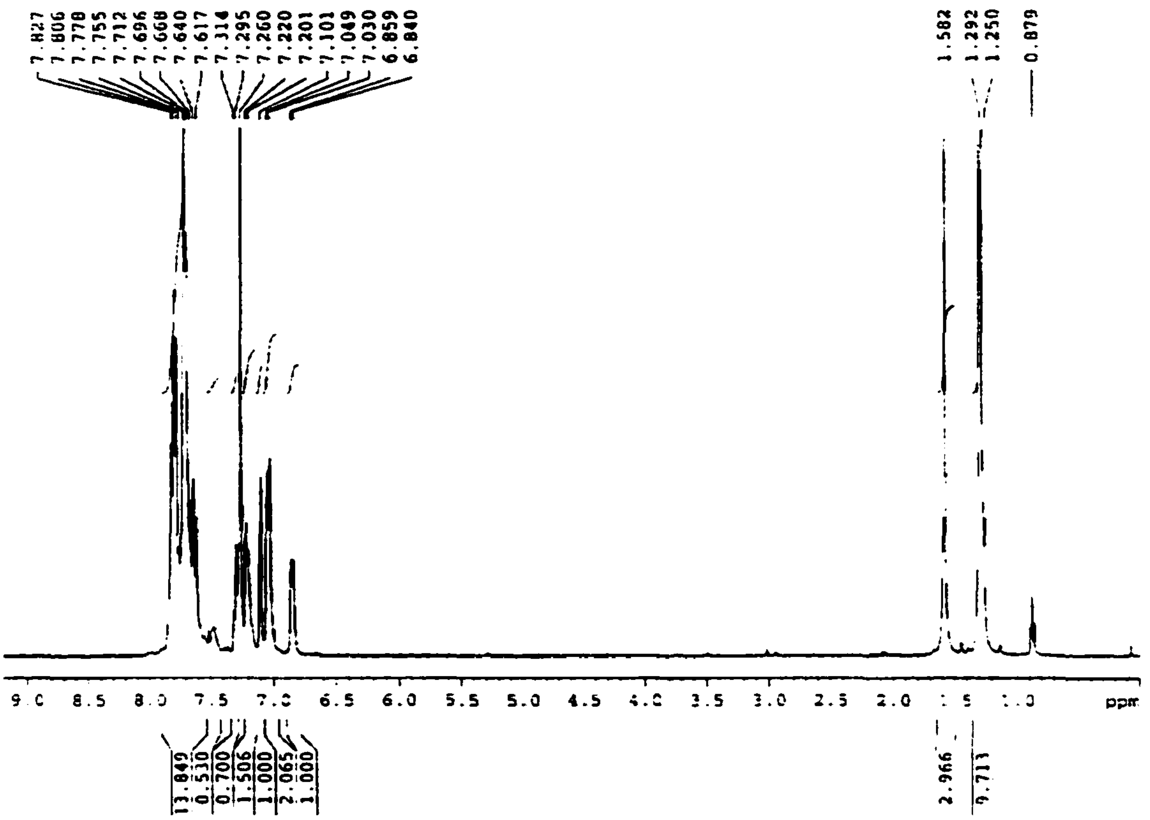
^{19}F NMR of poly(ethylene glycol)monomethylether (repeat unit average = 7) substituted PAPO (11).



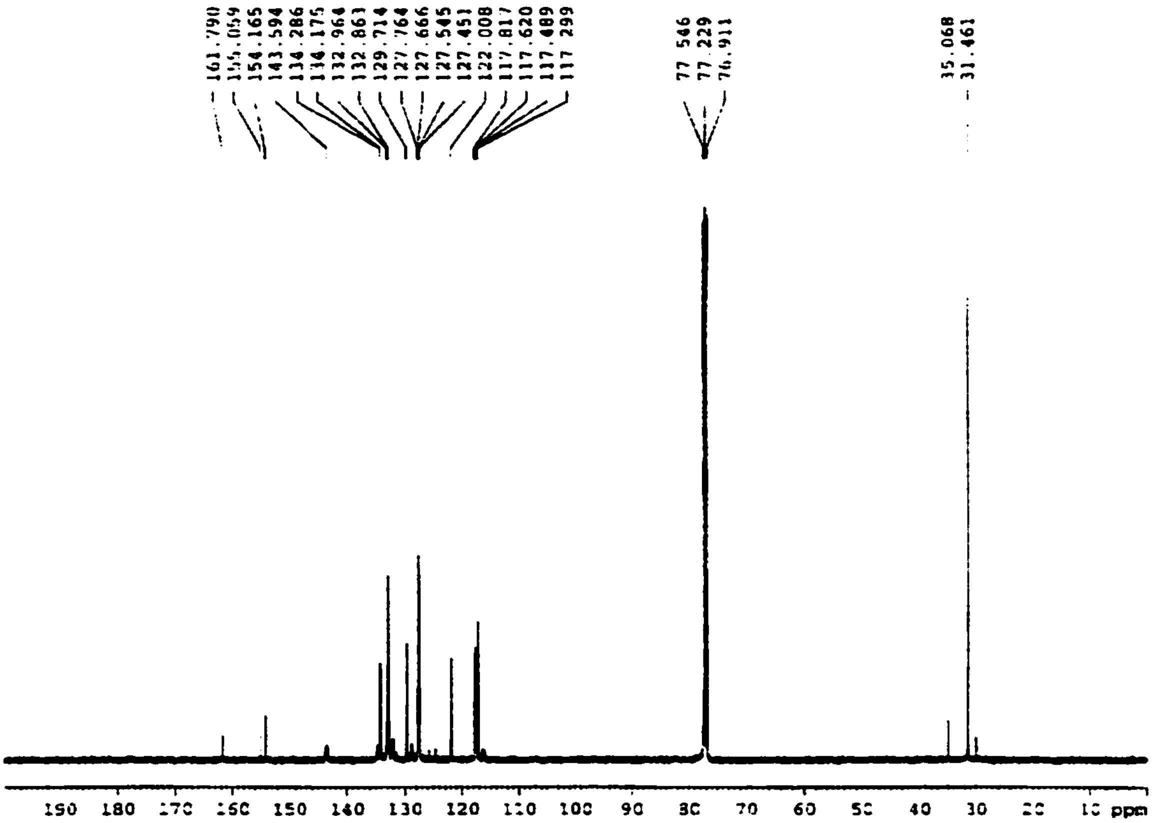
^{1}H NMR of 4-methylbenzylamine substituted PAPO (12).



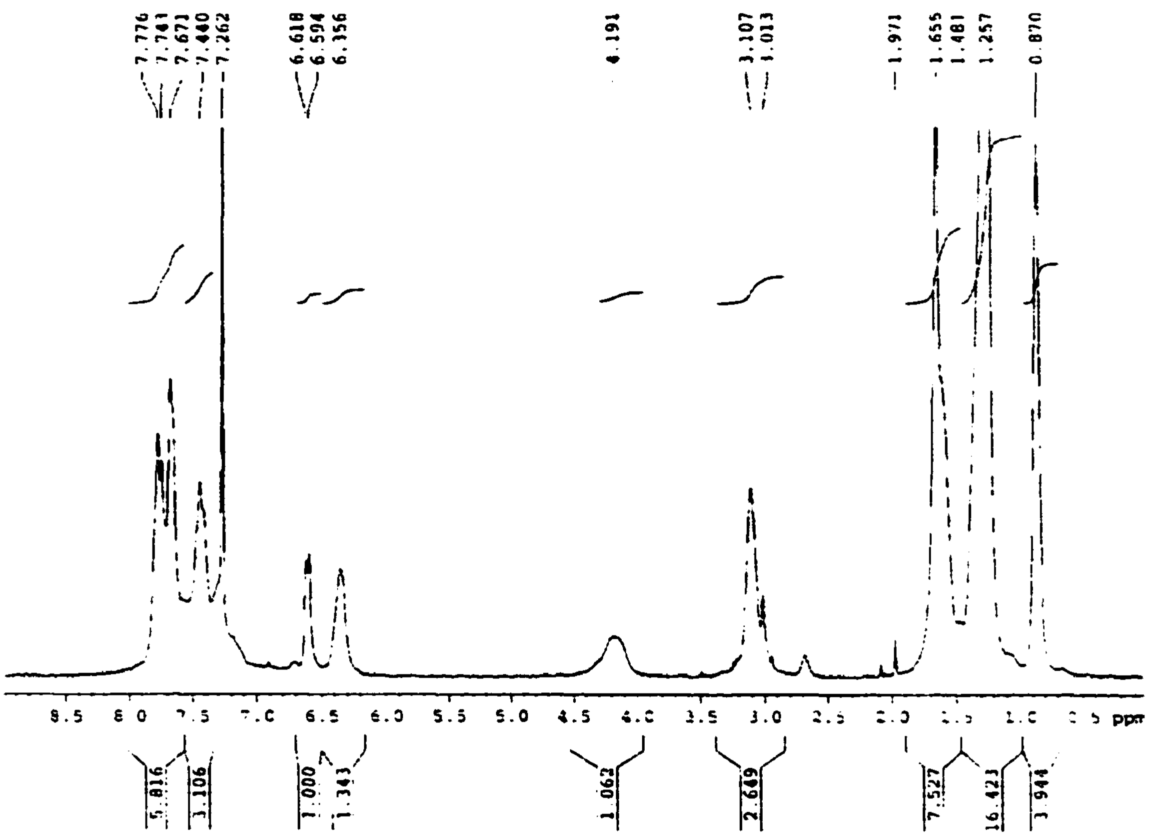
^{1}H NMR of 4-aminophenol substituted PAPO (13).



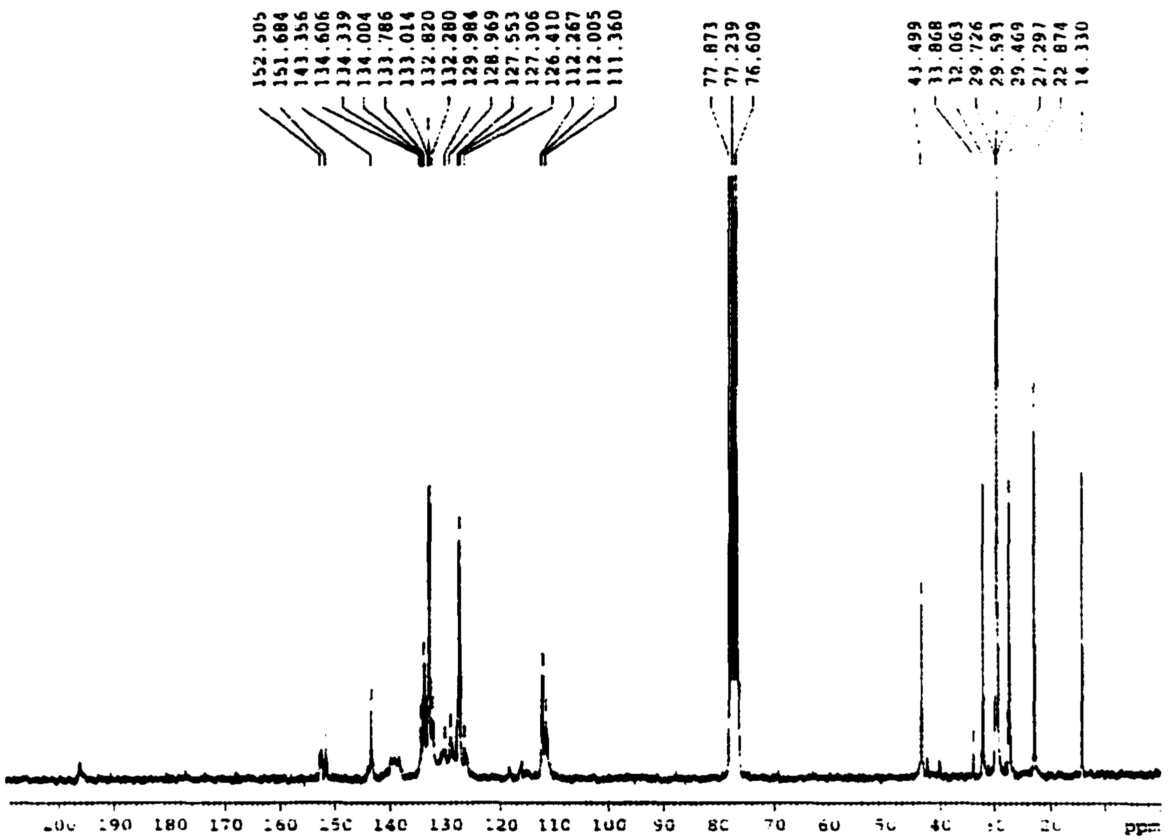
^{1}H NMR of 3-*t*-butylphenol substituted PAPO (14).



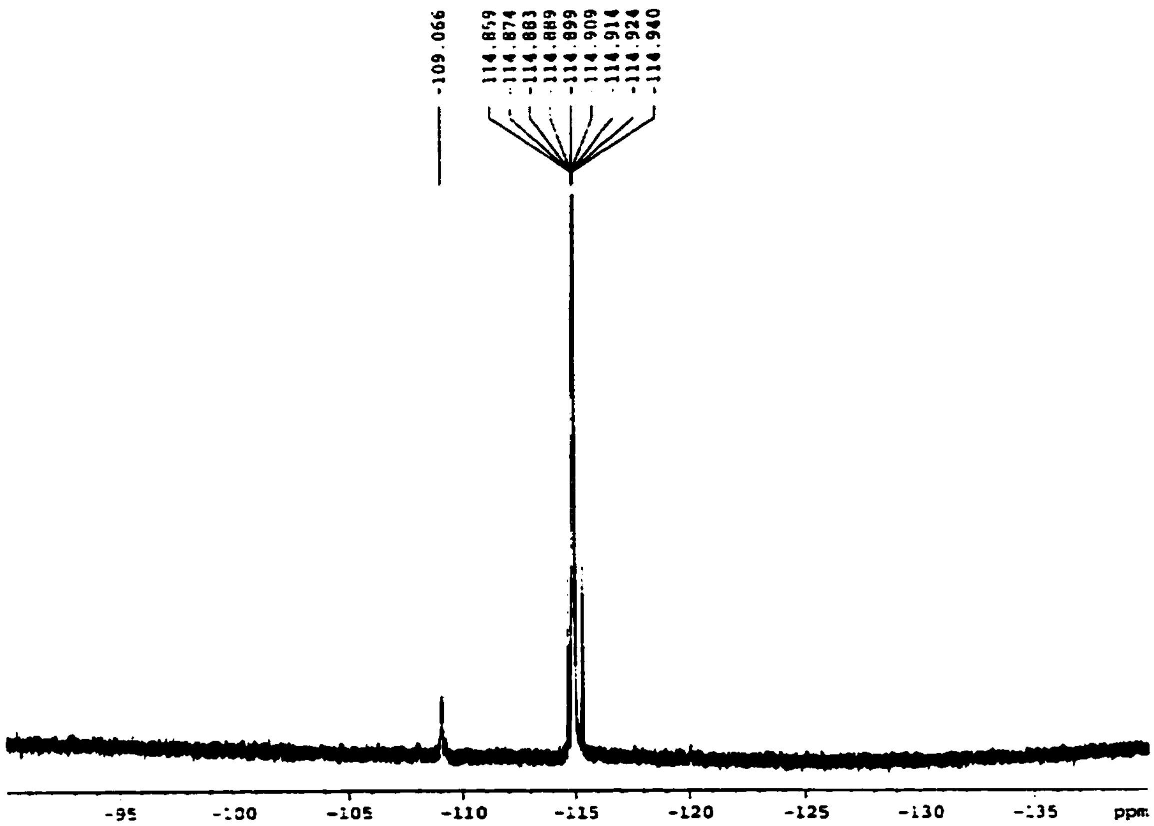
^{13}C NMR of 3-*t*-butylphenol substituted PAPO (14).



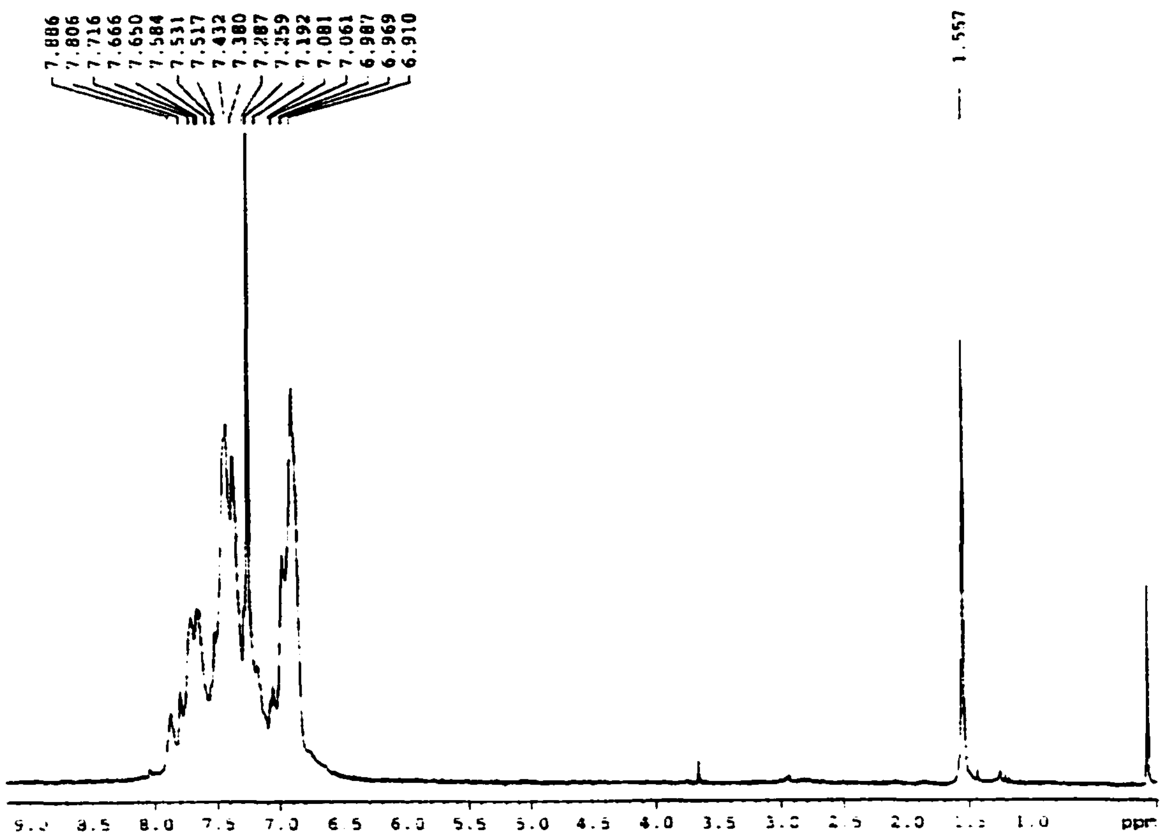
^{1}H NMR of *n*-nonylamine substituted PAPO-*co*-PPP (15).



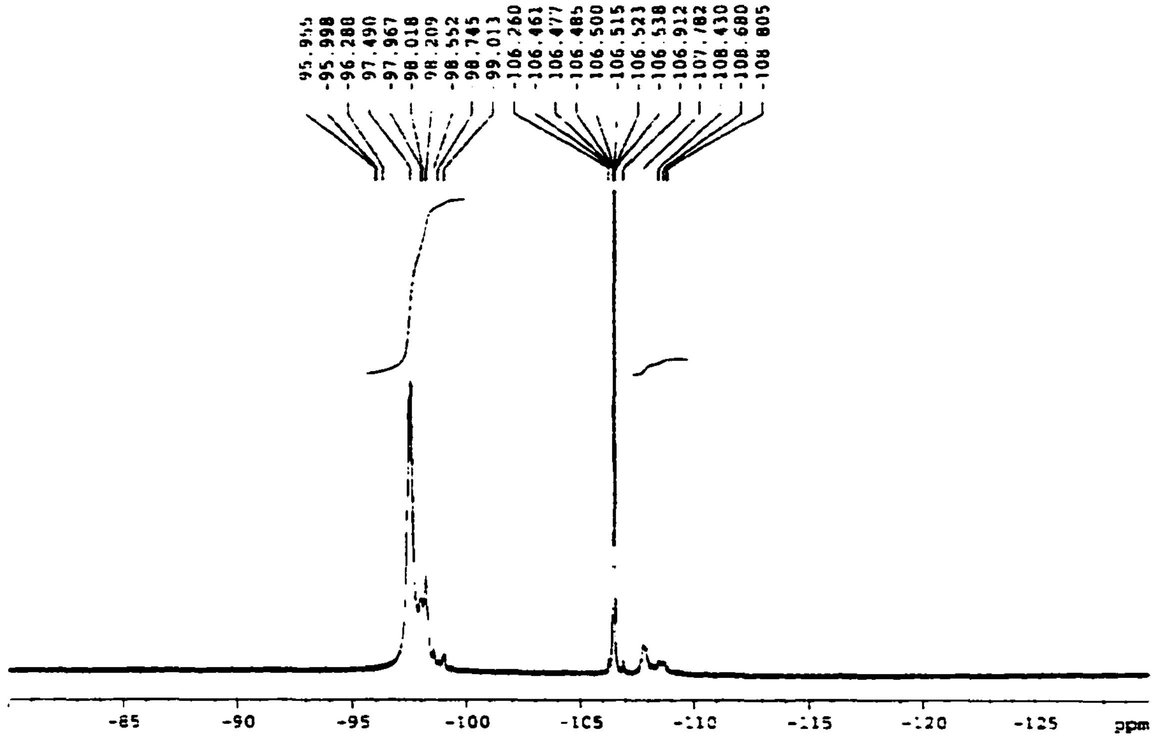
^{13}C of *n*-nonylamine substituted PAPO-*co*-PPP (15).



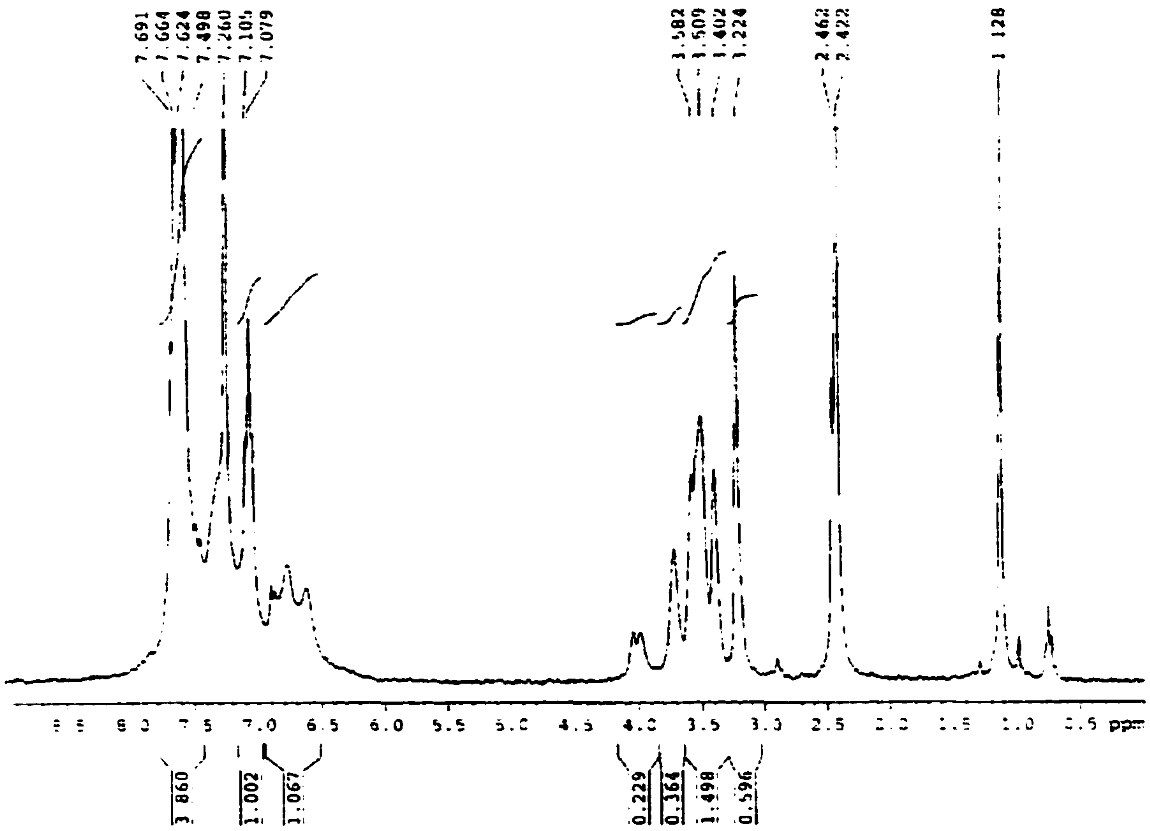
^{19}F NMR of *n*-nonylamine substituted PAPO-*co*-PPP (15).



^{1}H NMR of poly(4-fluorobenzophenone) (PPP).



^{19}F NMR of poly(4-fluorobenzophenone) (PPP).



^{1}H NMR of poly(ethylene glycol)monomethylether (repeat unit average = 7) substituted PAPO-*co*-PPP.

Millennium Sample Information

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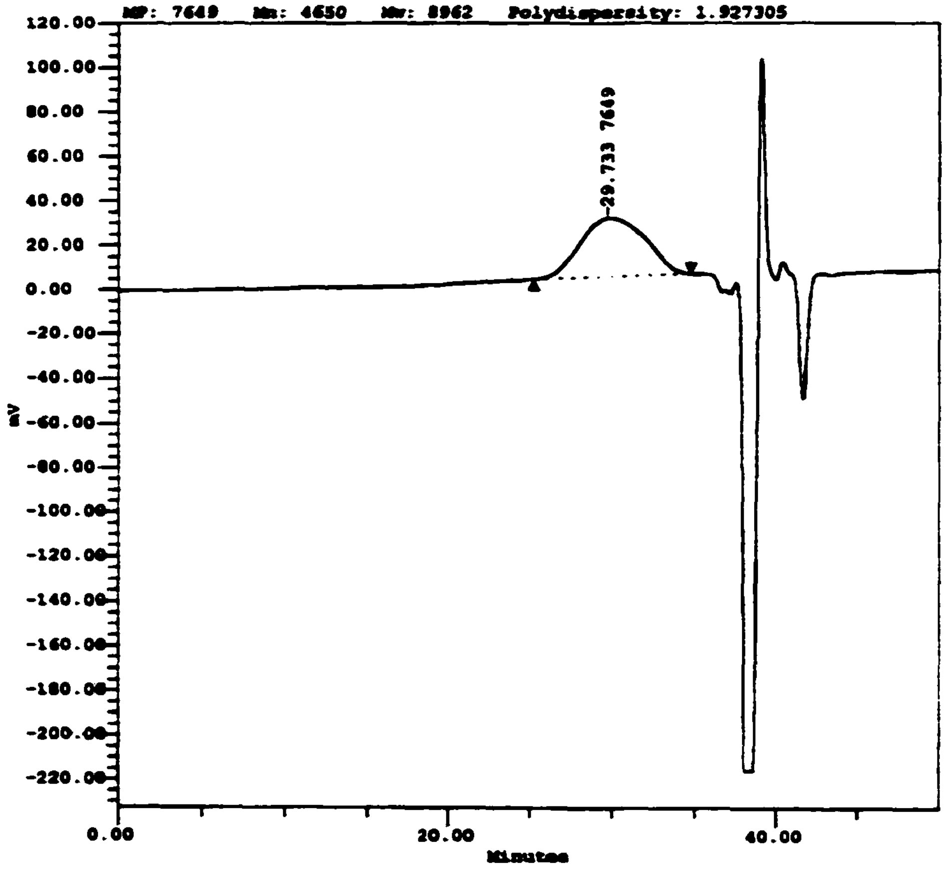
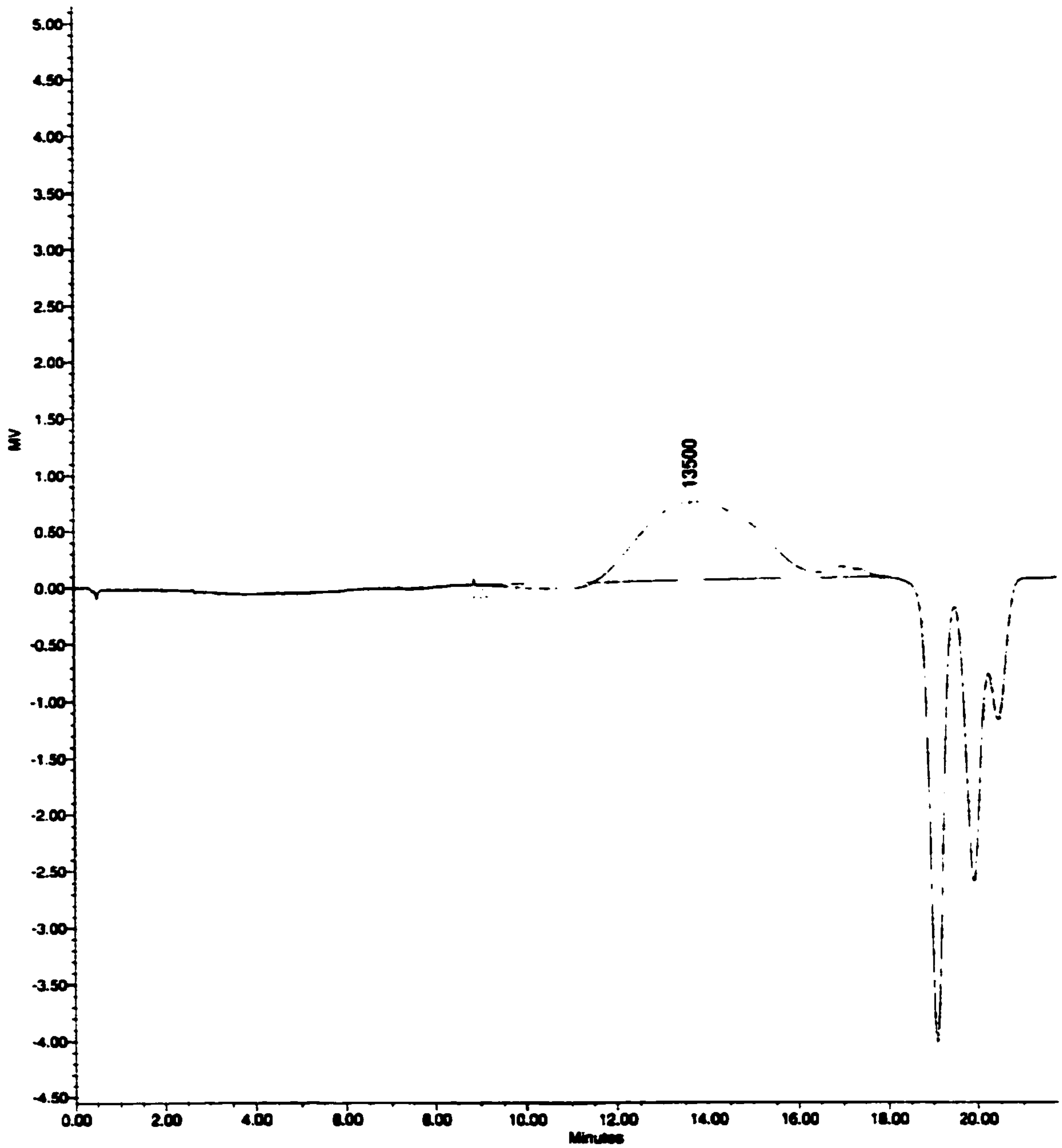
Sample Name: ls34b
Vial: 1
Injection: 2
Channel: SATIN
Date Acquired: 04/16/01 09:39:11 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: whitefishbay

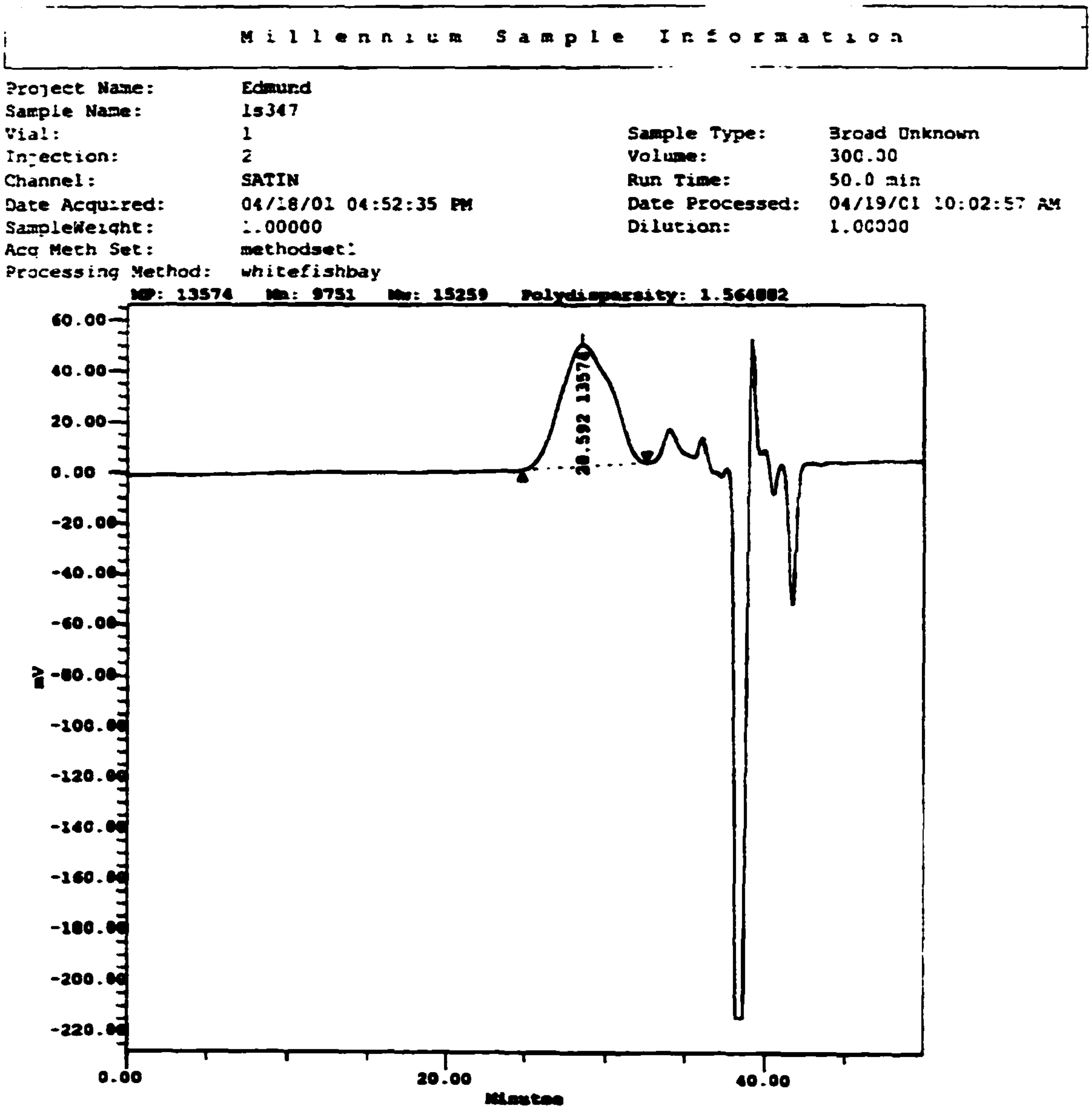
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/17/01 09:16:28 AM
Dilution: 1.00000



GPC of PAPO-*co*-PPP (7).



GPC of poly(PAPO-*co*-PPP) (8).



Millennium Sample Information

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Sample Name: ls347
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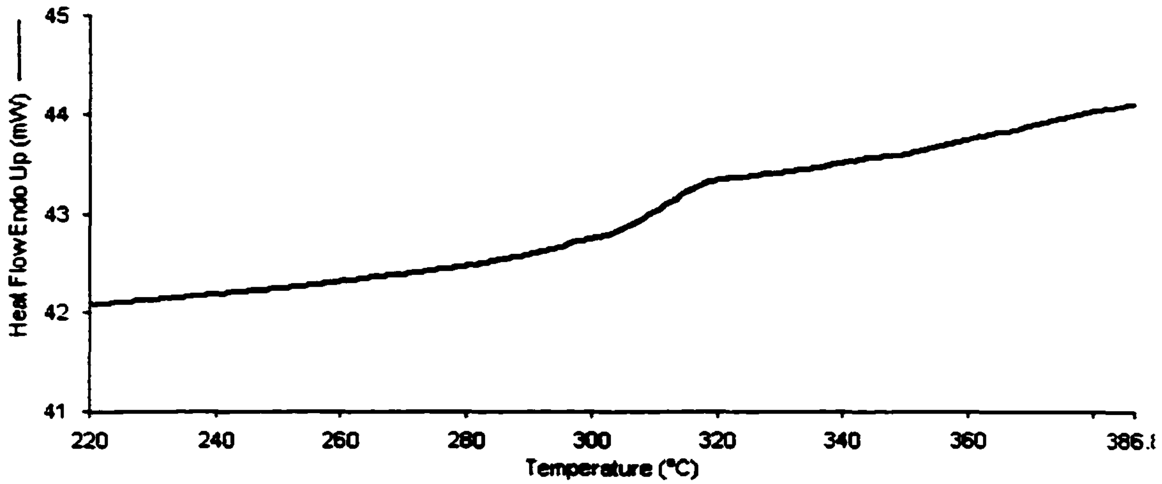
Injection: 2
Channel: SATIN
Date Acquired: 04/18/01 04:52:35 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: whitefishbay

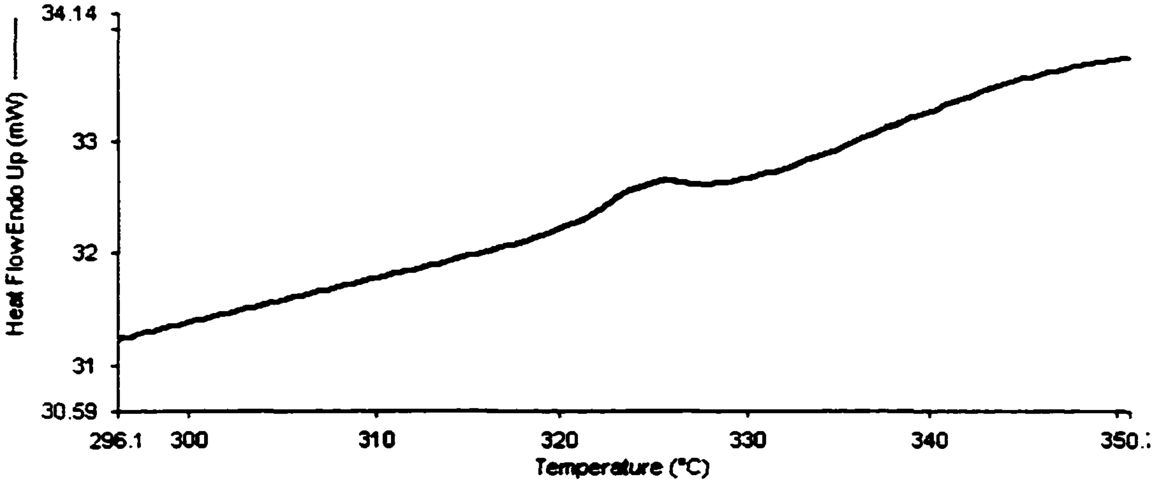
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 04/19/01 10:02:57 AM
Dilution: 1.00000

MP: 13574 Mn: 9751 Mw: 15259 Polydispersity: 1.564882

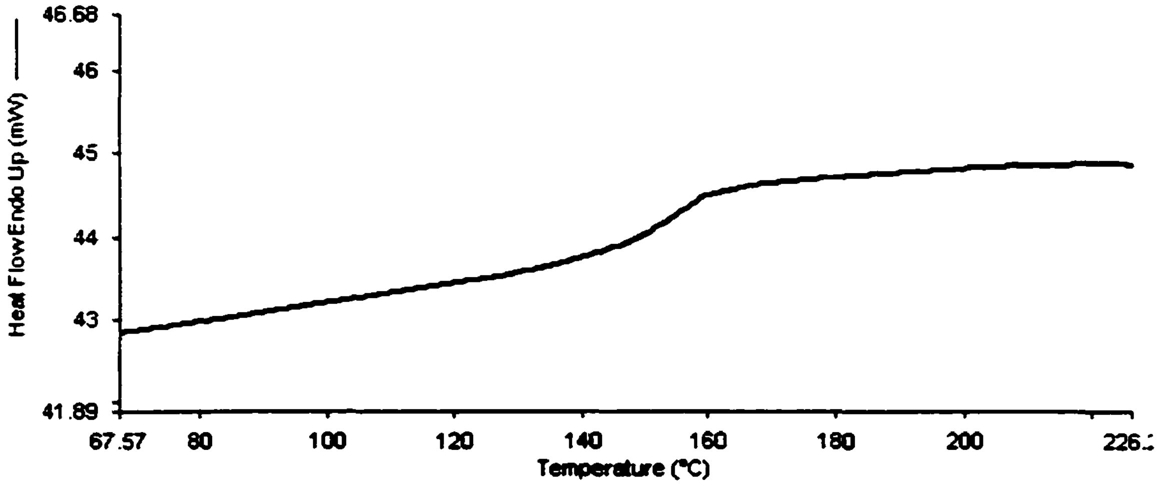
GPC of *n*-nonylamine substituted PAPO-*co*-PPP (15).



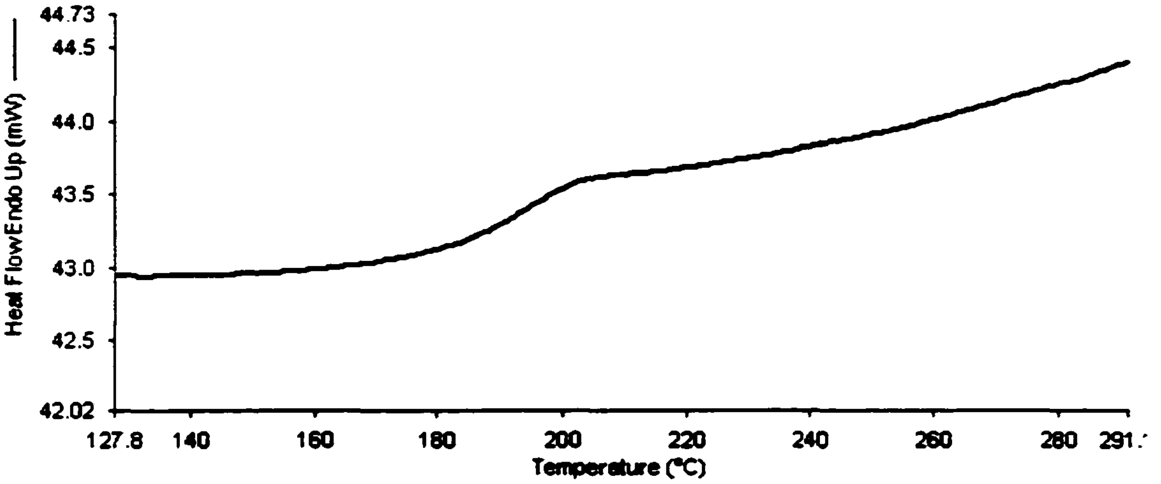
DSC of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (4).



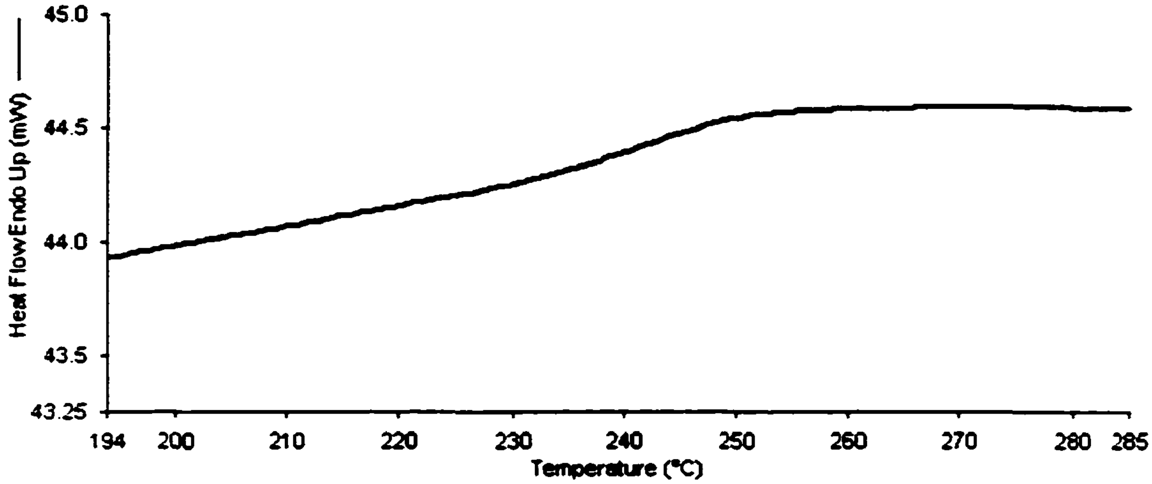
DSC of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (5).



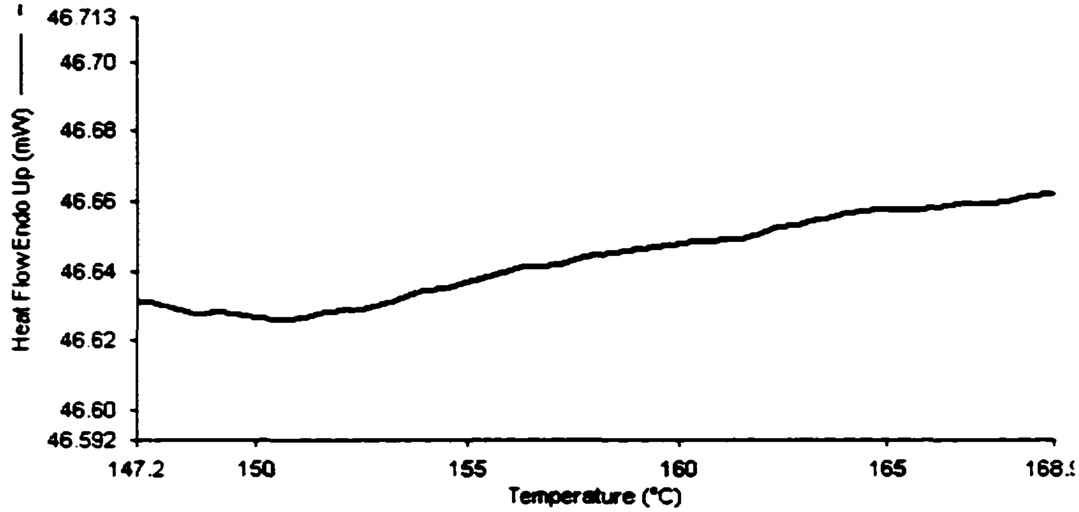
DSC of PAPO-*co*-PPP (7).



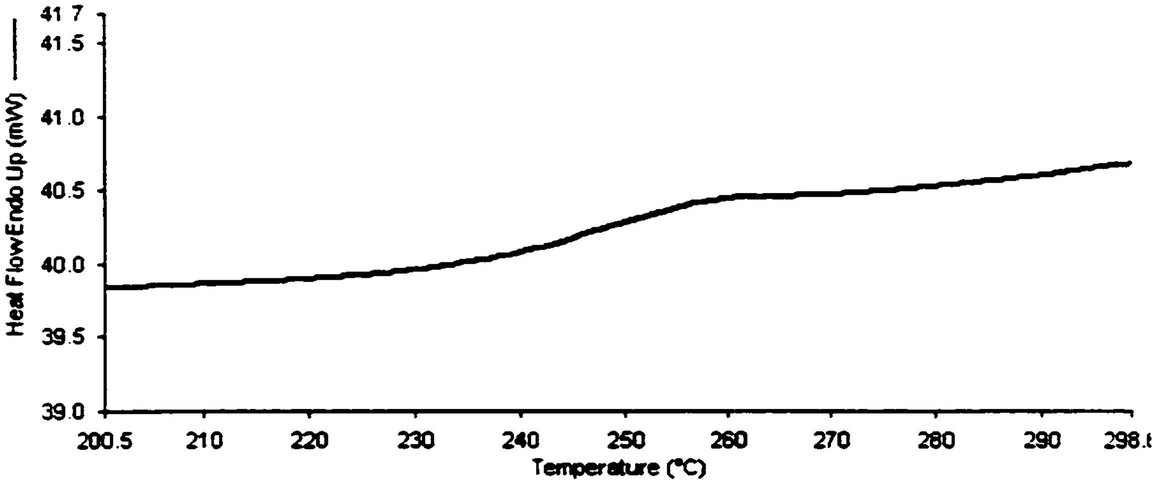
DSC of *n*-nonylamine substituted PAPO (9).



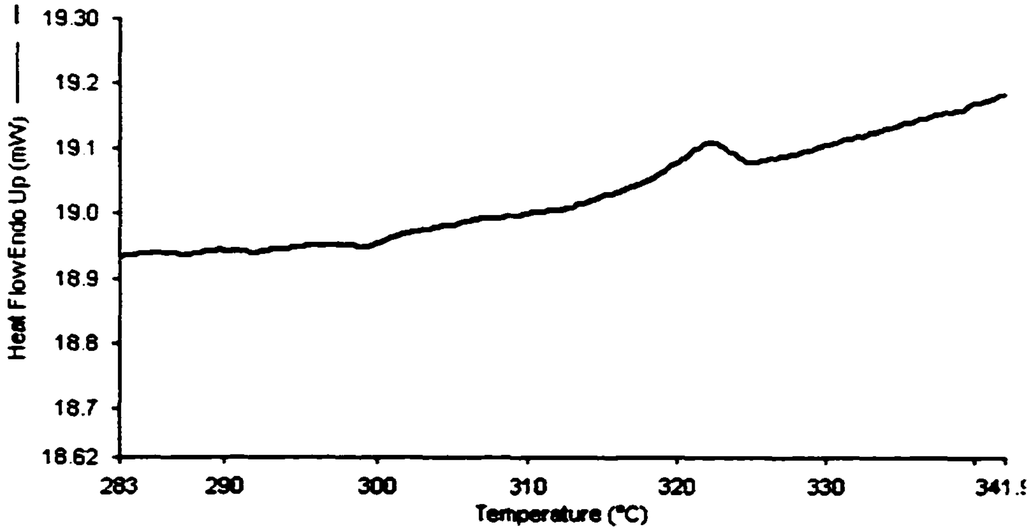
DSC of 4-*t*-butylphenol substituted PAPO (10).



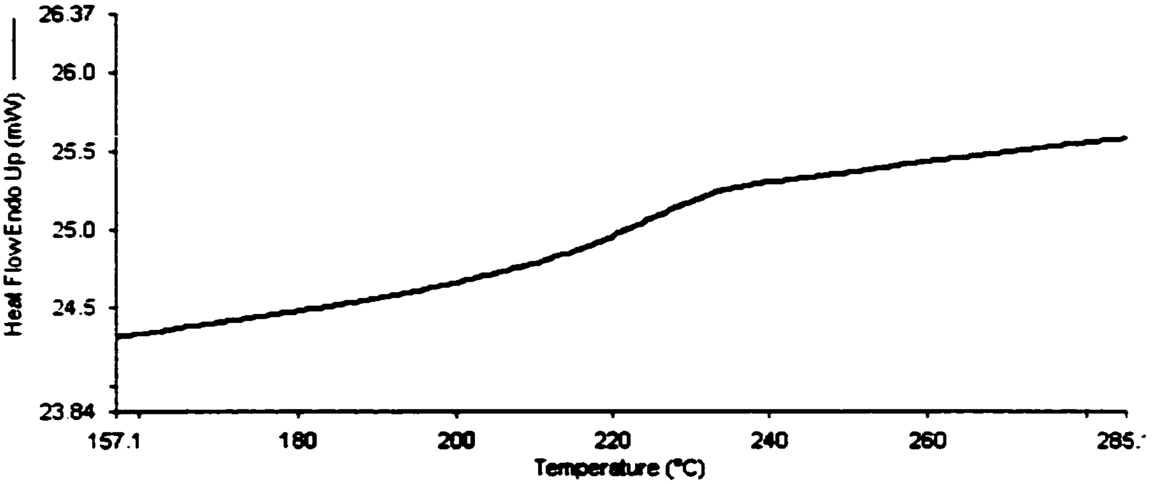
DSC of poly(ethylene glycol)monomethylether (repeat unit average = 7) substituted PAPO (11).



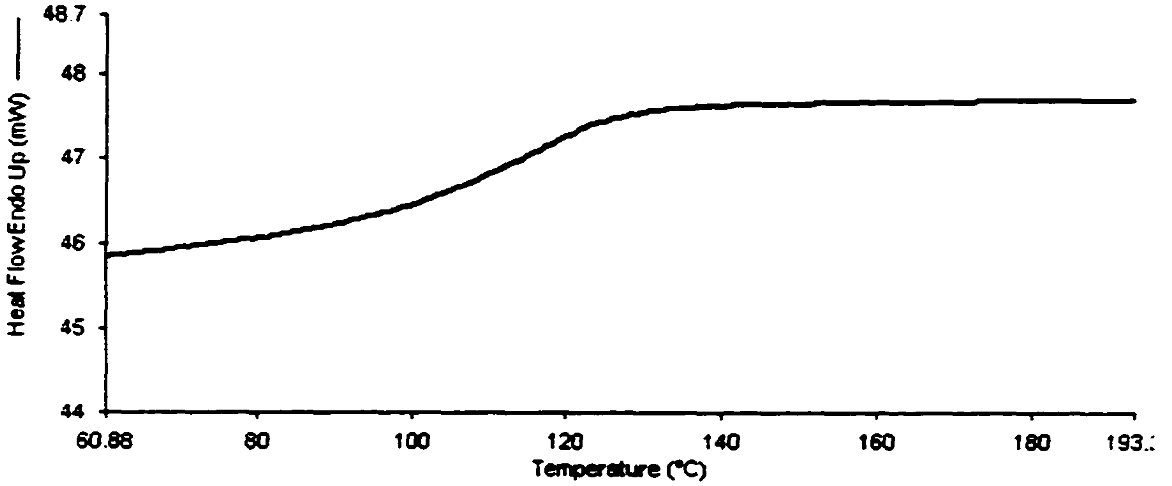
DSC of 4-methylbenzylamine substituted PAPO (12).



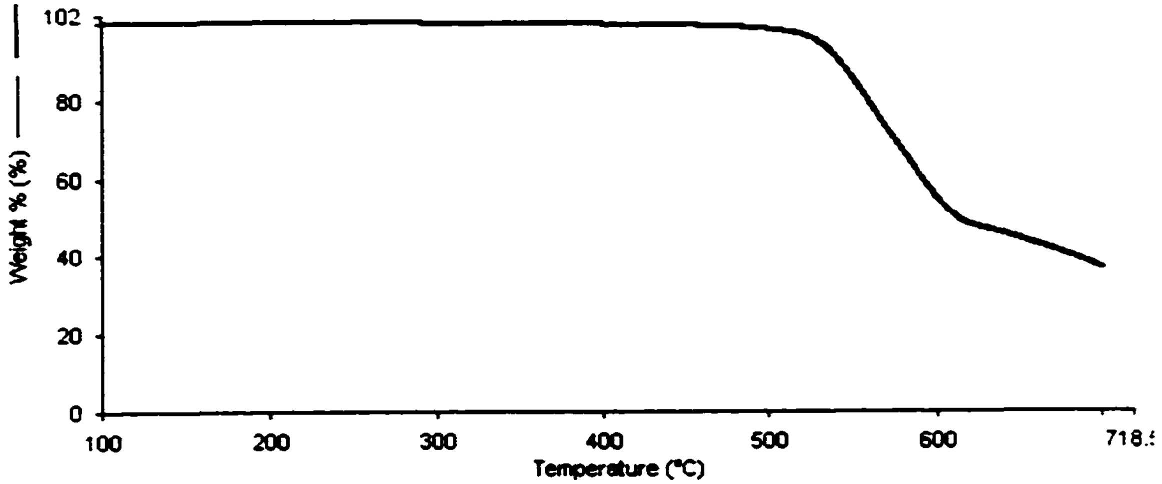
DSC of 4-aminophenol substituted PAPO (13).



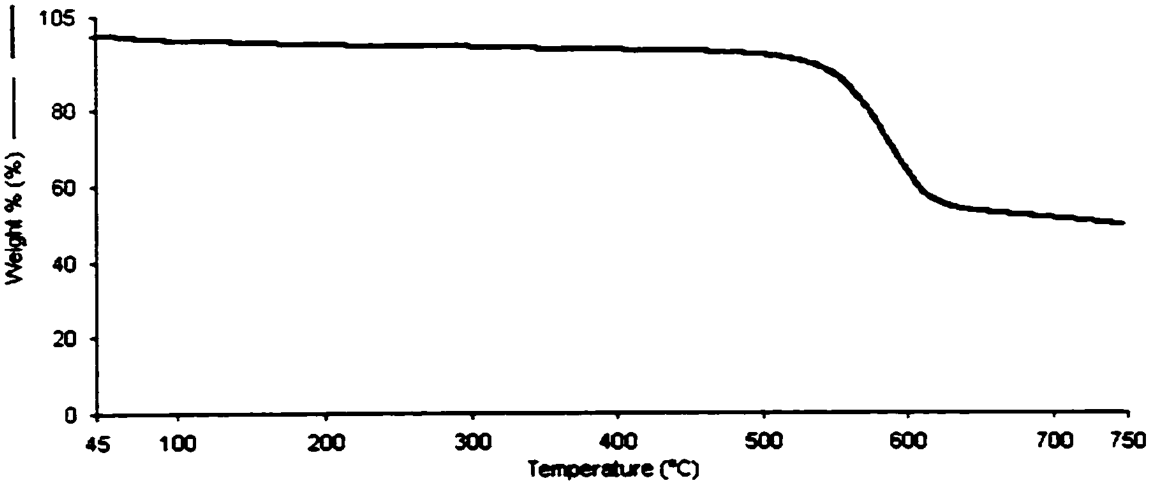
DSC of 3-*t*-butylphenol substituted PAPO (14).



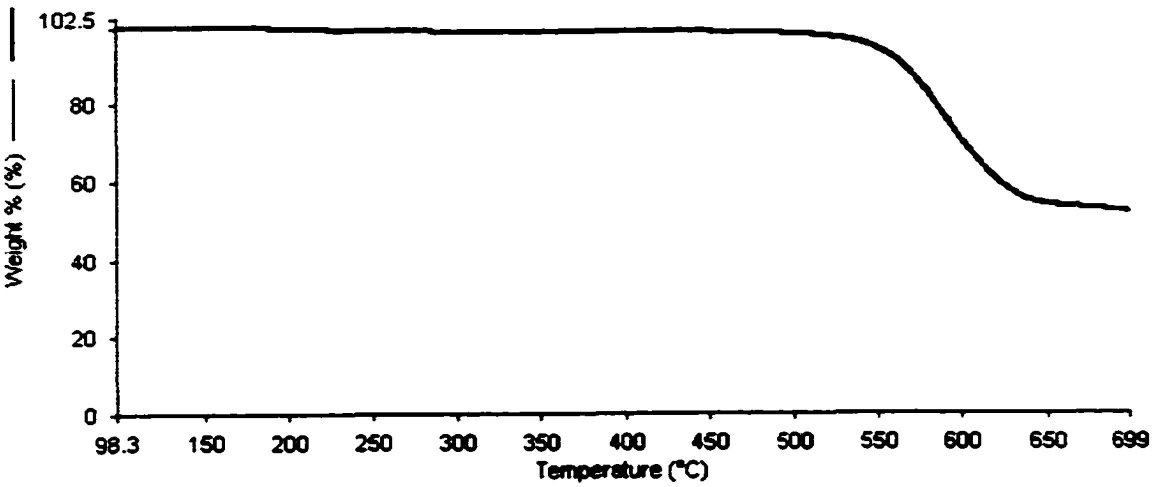
DSC of *n*-nonylamine substituted PAPO-*co*-PPP (15).



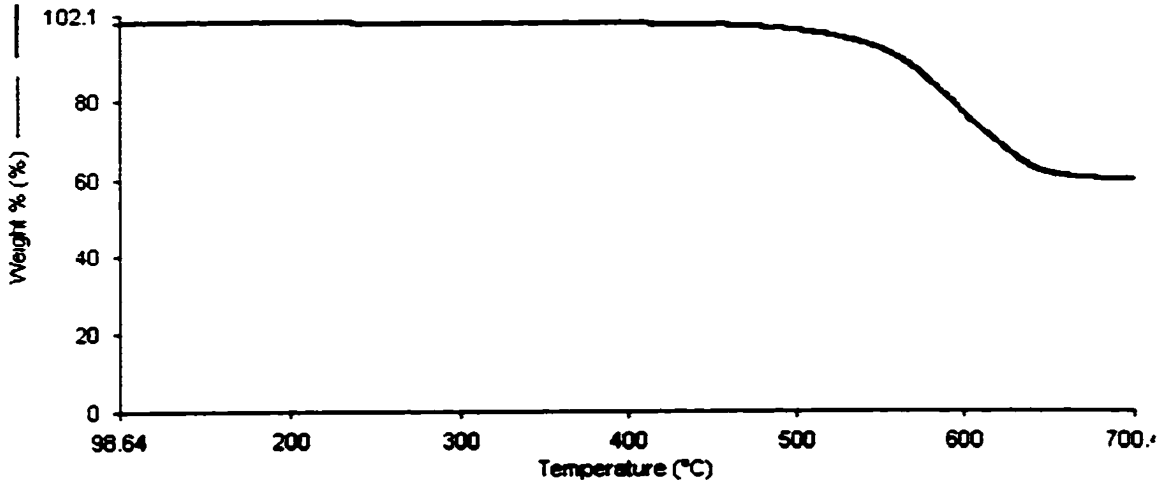
TGA in air of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (4).



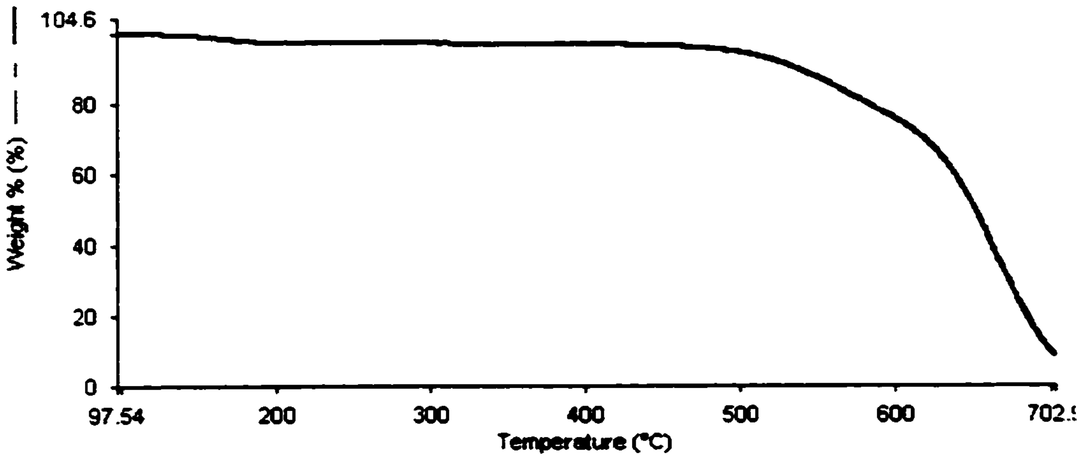
TGA in nitrogen of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (4).



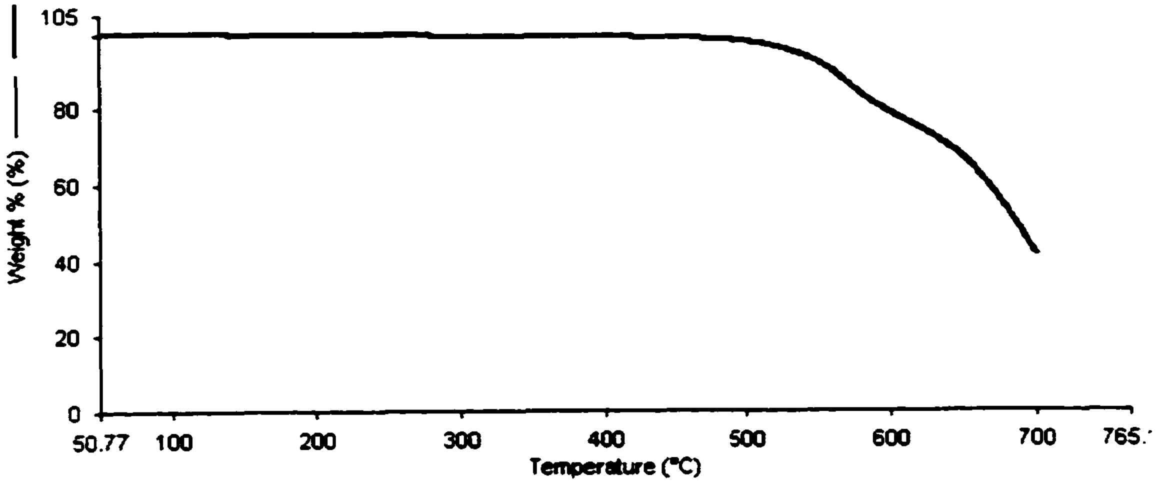
TGA in air of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (5).



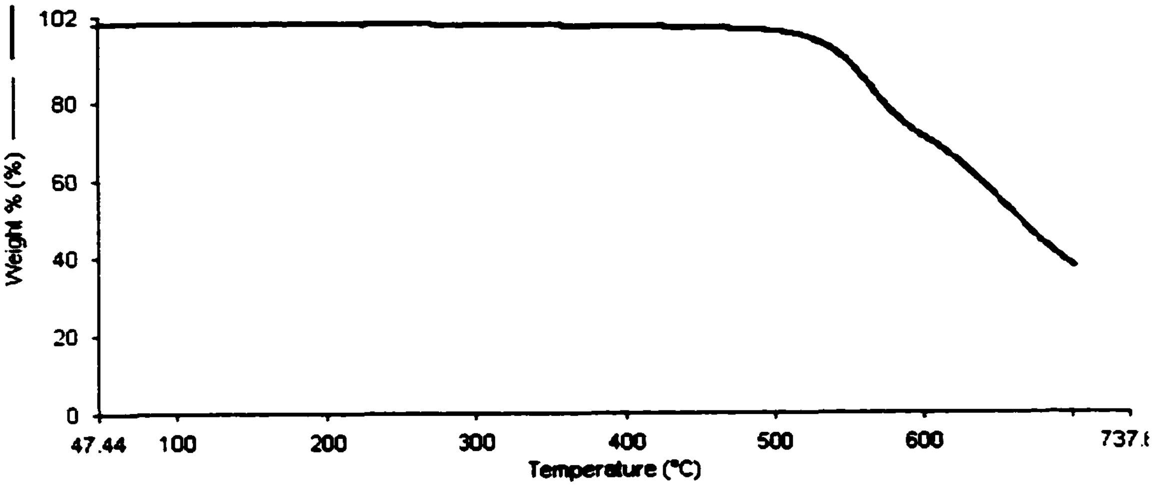
TGA in nitrogen of poly(4'-fluorophenyl-bis(4-phenyl)phosphine oxide) (5).



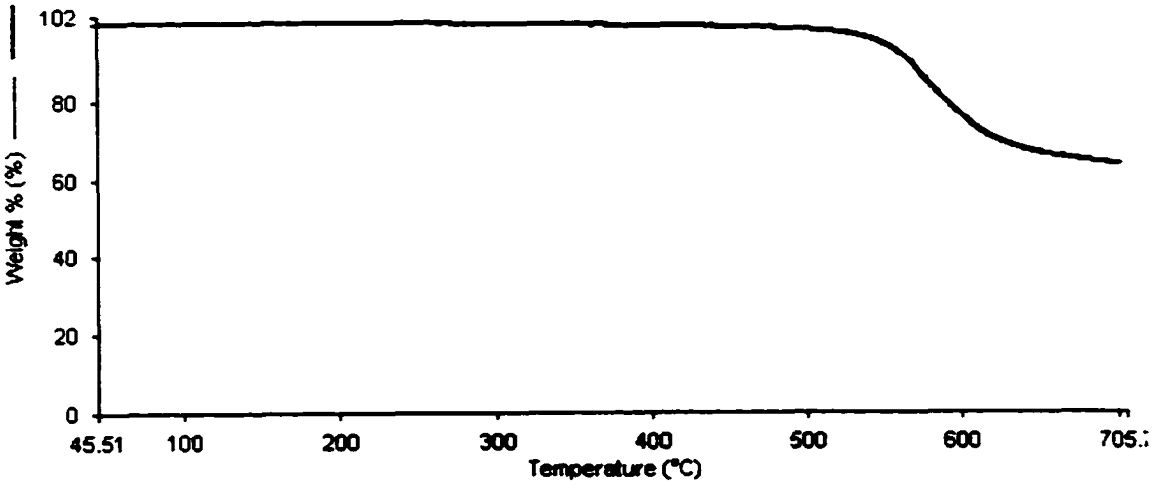
TGA in air of poly(PAPO-*co*-PPP) (7).



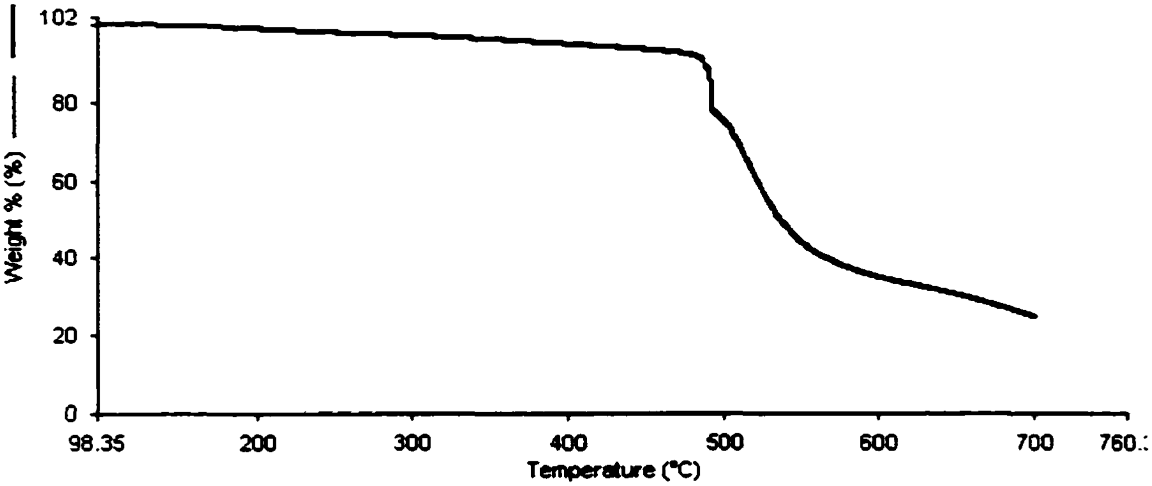
TGA in nitrogen of poly(PAPO-*co*-PPP) (7).



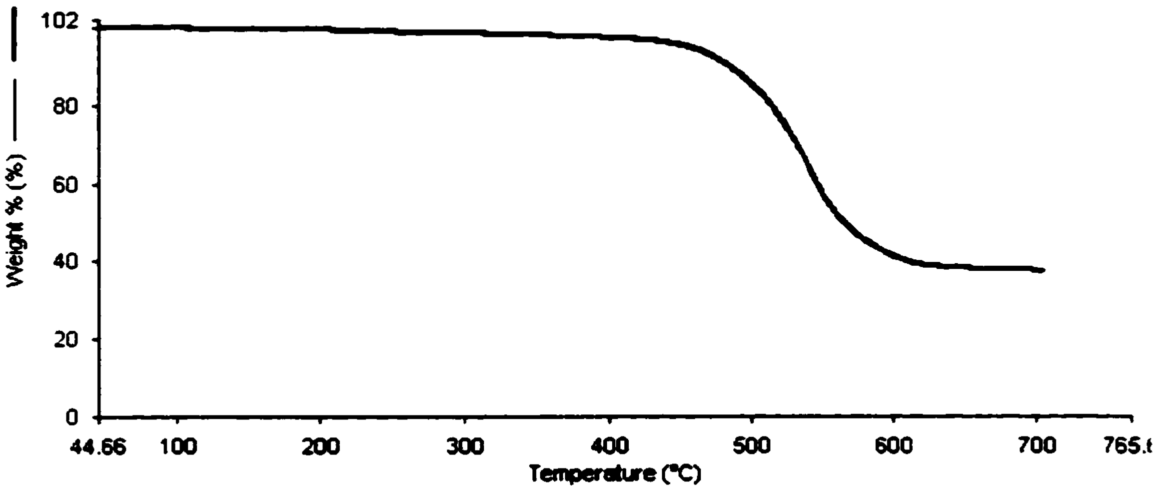
TGA in air of poly(PAPO-*co*-PPP) (8).



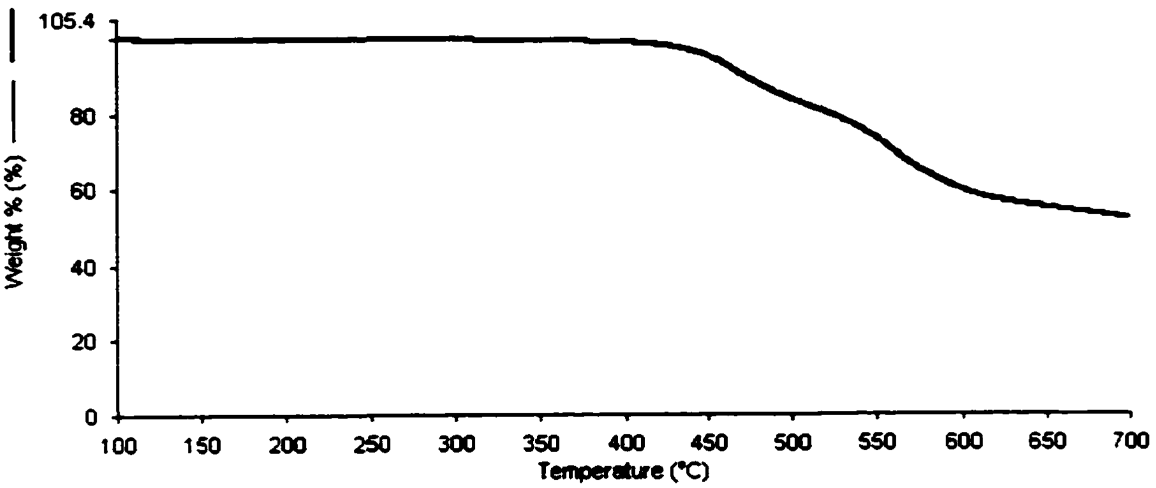
TGA in nitrogen of poly(PAPO-*co*-PPP) (8).



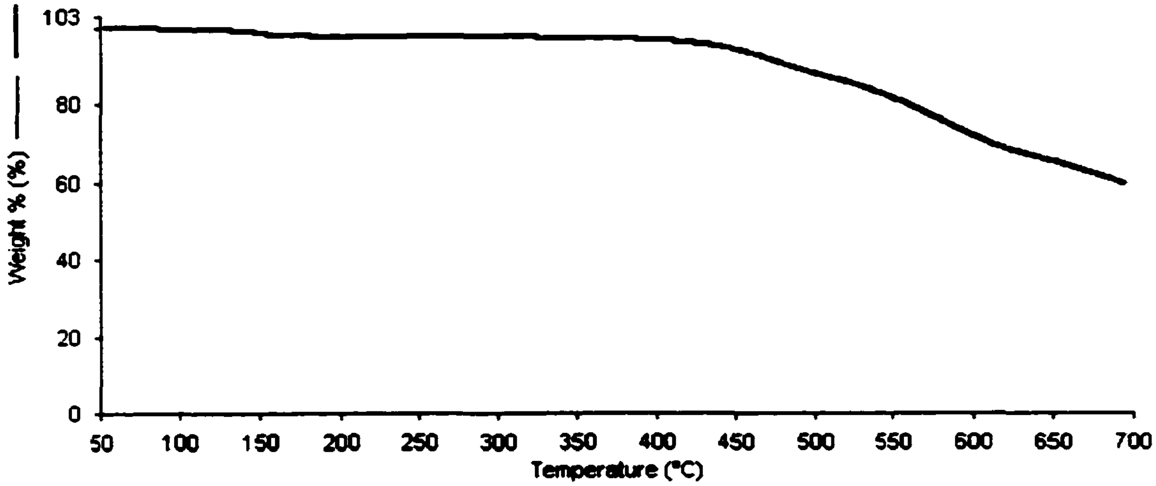
TGA in air of *n*-nonylamine substituted PAPO (9).



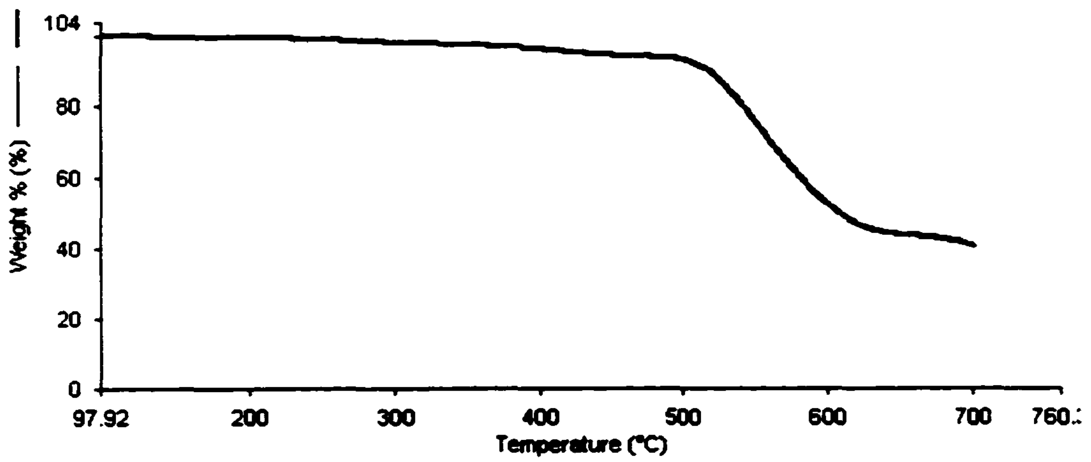
TGA in nitrogen of *n*-nonylamine substituted PAPO (9).



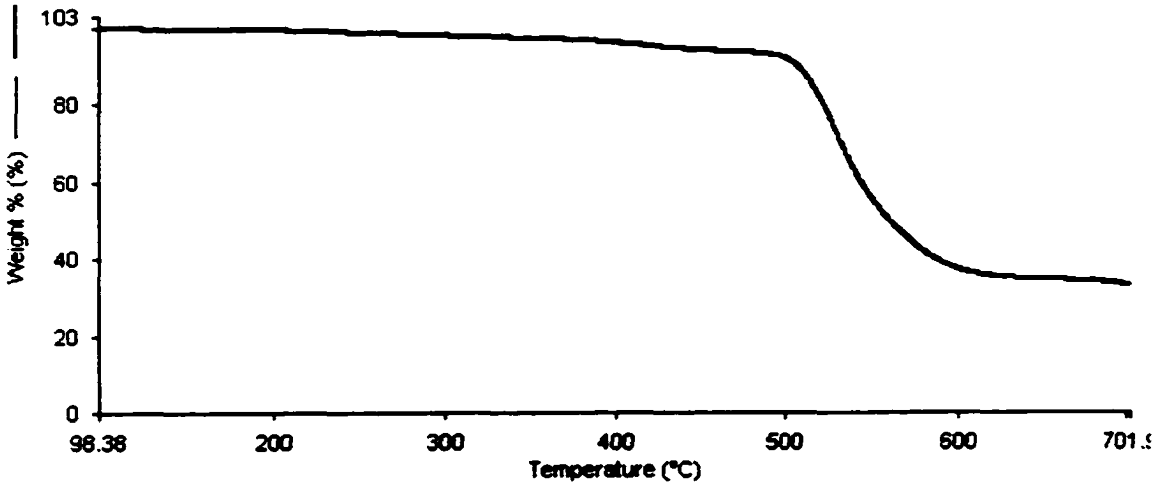
TGA in air of 4-*t*-butylphenol substituted PAPO (10).



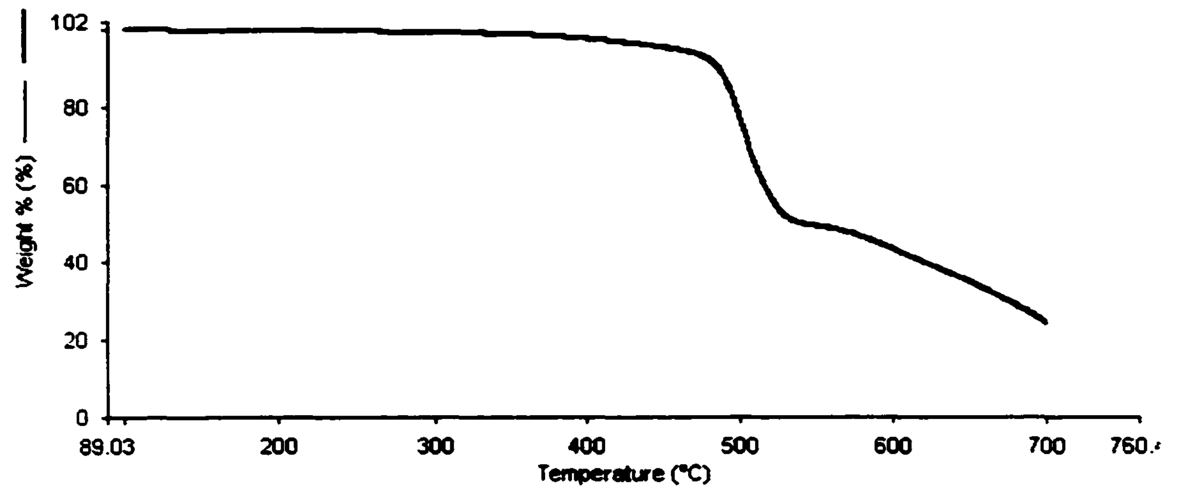
TGA in nitrogen of 4-*t*-butylphenol substituted PAPO (10).



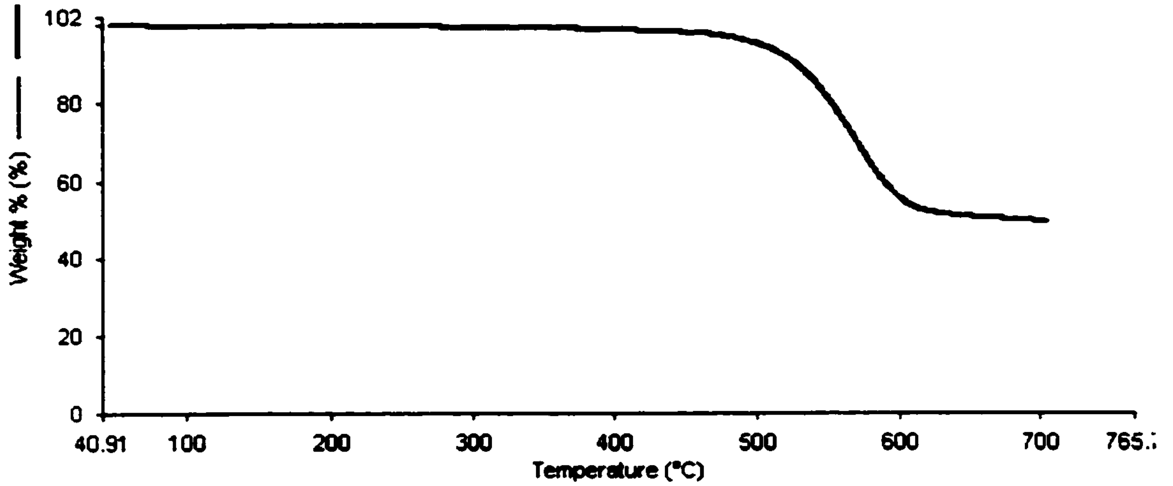
TGA in air of poly(ethylene glycol)monomethylether substituted PAPO (11).



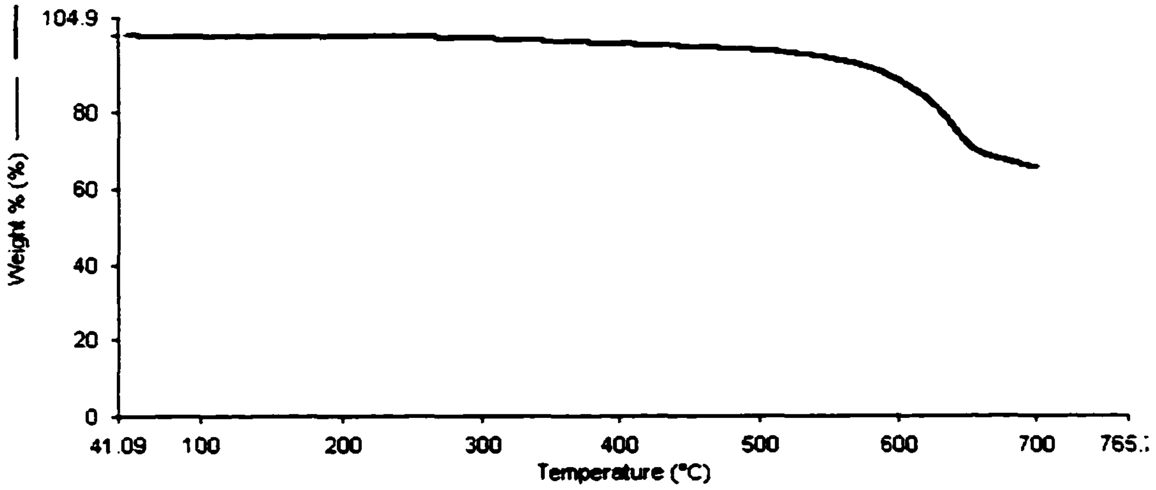
TGA in nitrogen of poly(ethylene glycol)monomethylether substituted PAPO (11).



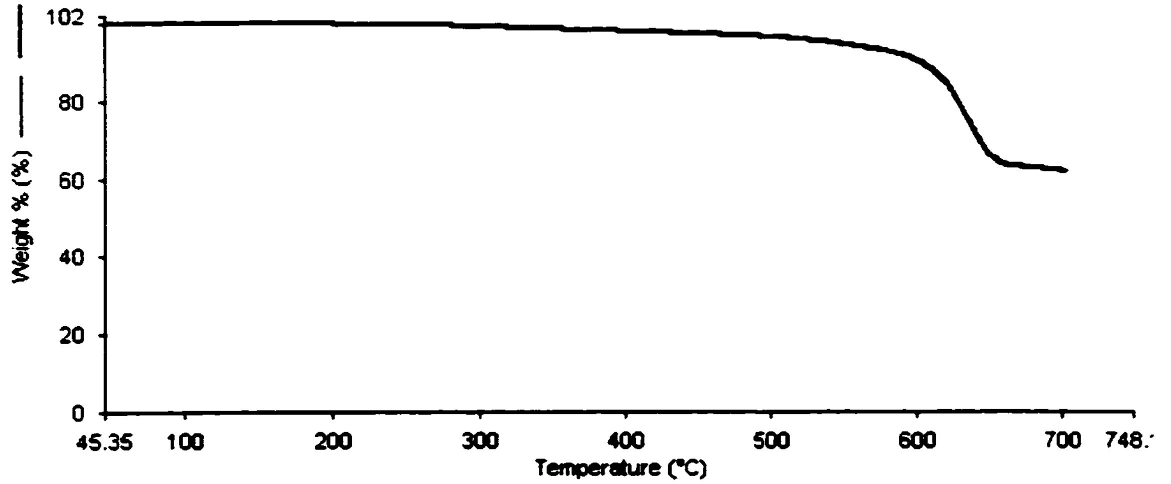
TGA in air of 4-methylbenzylamine substituted PAPO (12).



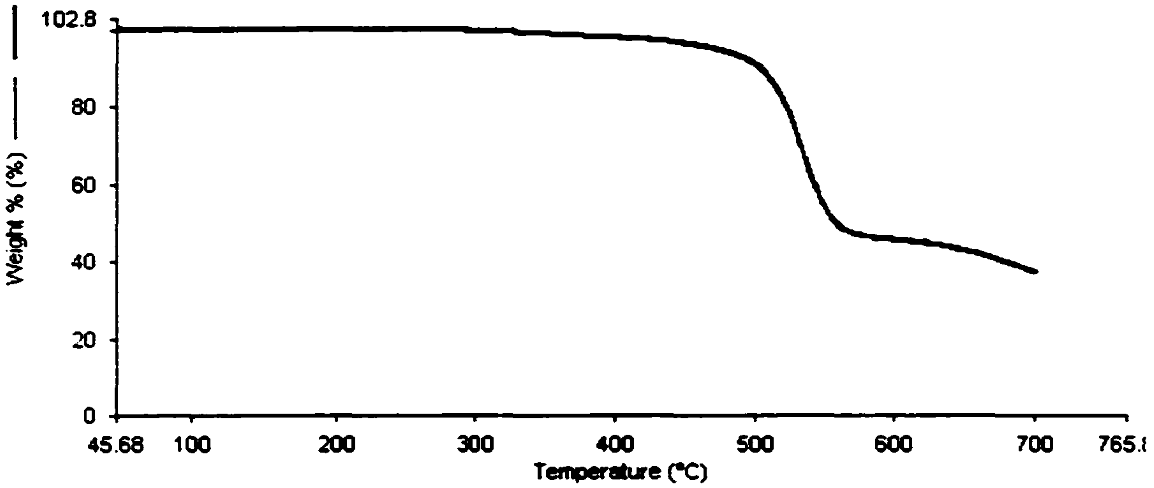
TGA in nitrogen of 4-methylbenzylamine substituted PAPO (12).



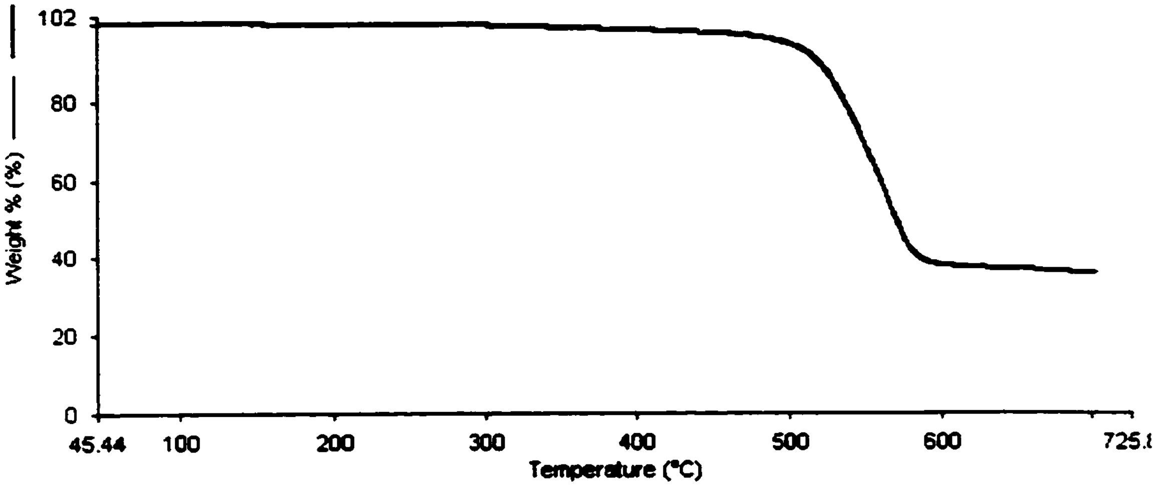
TGA in air of 4-aminophenol substituted PAPO (13).



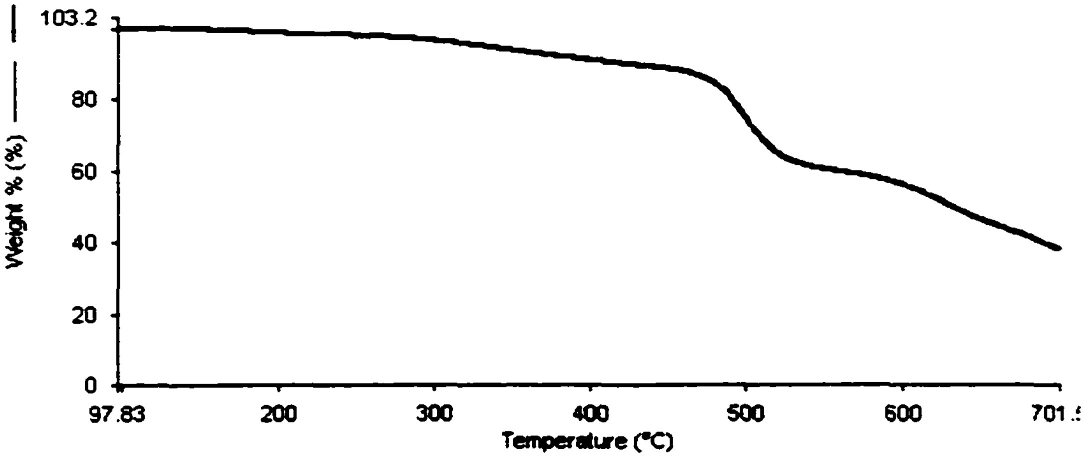
TGA in nitrogen of 4-aminophenol substituted PAPO (13).



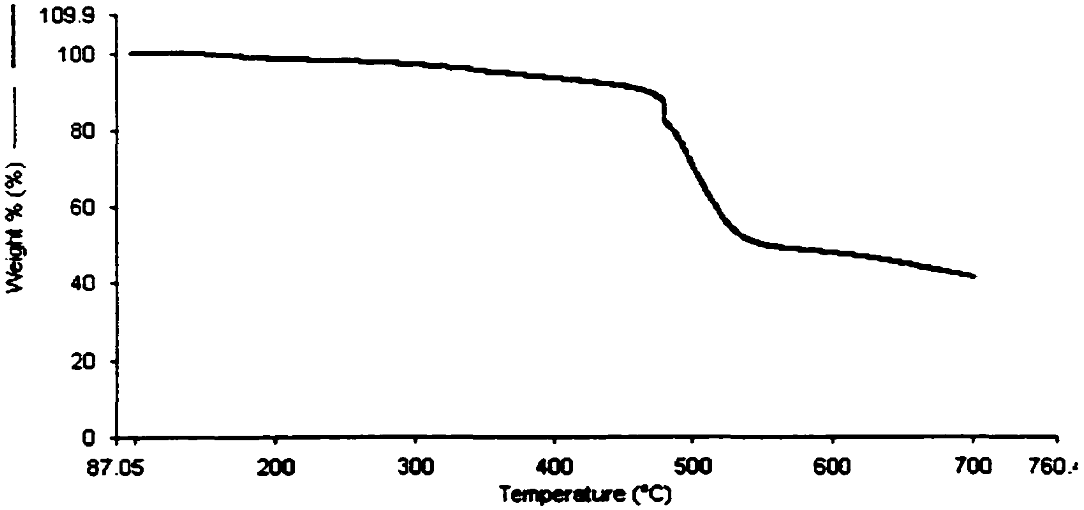
TGA in air of 3-*tert*-butylphenol substituted PAPO (14).



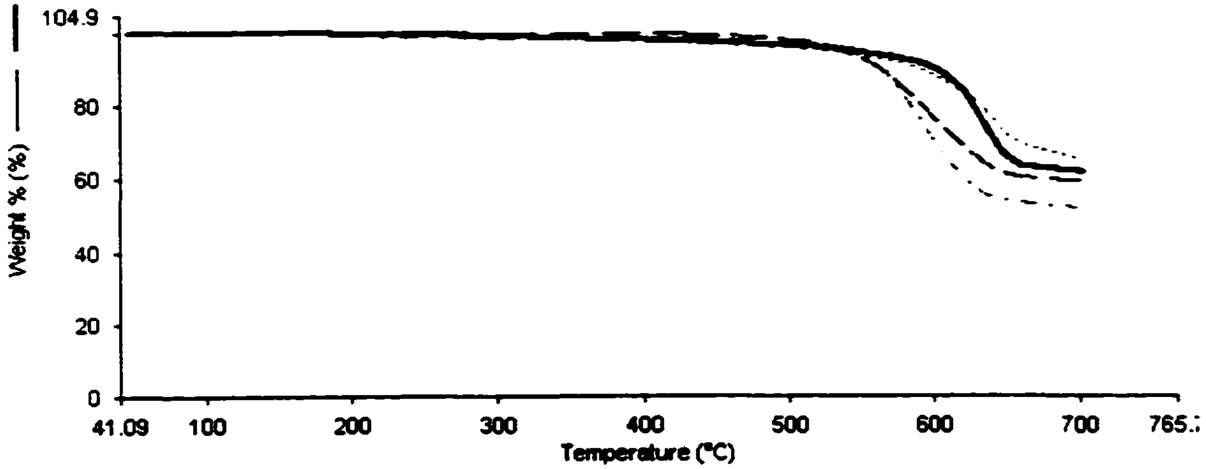
TGA in nitrogen of 3-*tert*-butylphenol substituted PAPO (14).



TGA in air of *n*-nonylamine substituted poly(PAPO-*co*-PPP) (15).



TGA in nitrogen of *n*-nonylamine substituted poly(PAPO-*co*-PPP) (15).



TGA of PAPO (5) in air (— — —), in nitrogen (— · — ·), 4-aminophenol substituted PAPO (13) in air (·····) and in nitrogen (———).