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Synthesis and free radical polymerization of disubstituted functionalized 1,3-butadienes

by

Melissa Kay Murphy

A thesis submitted to the graduate faculty
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Program of Study Committee:
Valerie V. Sheares (Major Professor)
Dennis Johnson
Richard Larock

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This is to certify that the Master's thesis of

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has met the thesis requirements of Iowa State University

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ABBREVIATIONS

AIBN	2,2'-Azobisisobutyronitrile
ATRP	Atom Transfer Radical Procedures
BHT	2,6-Di-*tert*-butyl-4-methylphenol
$CHCl_3$	Chloroform
CH_2Cl_2	Dichloromethane
CPBD	2,3-Bis(cyanopropyl)-1,3-butadiene
d	Doublet
DBE	1,2-Dibromoethane
dd	Doublet of doublets
DSC	Differential Scanning Calorimetry
EOBD	2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene
GC	Gas Chromatograph
GPC	Gel Permeation Chromatograph
IR	Infrared
m	Multiplet
$\langle M_n \rangle$	Number Average Molecular Weight
$\langle M_w \rangle$	Weight Average Molecular Weight
MHz	Megahertz
MS	Mass spectrometry
NBR	Nitrile Rubber
NMR	Nuclear Magnetic Resonance

ppm	Parts Per Million
PDI	Polydispersity Index
PS	Polystyrene
q	Quartet
s	Singlet
SBR	Styrene Butadiene Rubber
S_N2	Nucleophilic Substitution
S_N2'	Nucleophilic Substitution Bimolecular
t	Triplet
T_g	Glass Transition Temperature
TEMPO	2,2,6,6-tetramethylpiperidinoxy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran

GENERAL INTRODUCTION

More than 70% of all elastomeric materials produced each year are synthetic. Of this synthetic rubber, Styrene-Butadiene Rubber (SBR) is the principle elastomer made. SBR is made by emulsion copolymerization of styrene (25%) and butadiene (75%) at a rate of over 1 million tons per year. Another elastomer produced in large quantities (200 million pounds per year) is Nitrile Rubber (NBR), which is a copolymer of acrylonitrile and butadiene. Although SBR and NBR make up the majority of the elastomeric materials, they are limited by their properties. In order to vary the applications of the materials, it is necessary to incorporate different properties. One such way to give polymeric materials new properties is to blend two polymers together. This method is simple and can combine the properties of the two different materials, but oftentimes the materials do not combine well and lead to product failure. A number of ways have been explored to overcome this problem, including the use of compatabilizers such as graft copolymers and block copolymers.

Our group chose a different approach to solving the problem of incorporating various properties into elastomeric materials. Through the approach of synthesizing a functionalized diene-based monomer and copolymerizing it with commercially important monomers such as styrene, we hope to produce polymers that contain the elastomeric properties of butadiene rubber, but gain new properties such as solvent resistance, increased thermal stability and improved mechanical properties. The moieties that our group has incorporated into the backbones of polybutadienes through the functionalization of monomers include nitrile, ester, carboxylic acid, hydroxy and amino groups. In this thesis, the synthesis of disubstituted functionalized diene-based monomers, the free radical homopolymerization and copolymerization of 2,3-bis(cyanopropyl)-1,3-butadiene and the controlled free radical polymerization of 2,3-bis(4-ethoxy-4oxobutyl)-1,3-butadiene will be discussed.

Thesis Organization

This thesis is divided into two chapters. The chapters are written in the style of a journal article. Each paper is presented with its own introduction, experimental, results and discussion, conclusion, acknowledgement and reference sections. Chapter 1 has been submitted to the journal *Macromolecules*. Following the last chapter is a general conclusion.

Chapter 1 describes the synthesis and free radical polymerization of 2,3-bis(cyanopropyl)-1,3-butadiene. The monomer was synthesized in a three-step synthesis involving the formation of an organozinc complex followed by an S_N2' reaction mediated by Cu(I) salts to form the respective functionalized dienes. Free radical polymerization produced moderate molecular weight materials at short reaction times with high solvent resistance resulting in characterization difficulties. As a result of these limitations, the copolymerizations of CPBD became more interesting. The solution copolymerization of 2,3-bis(cyanopropyl)-1,3-butadiene with styrene was examined first. This resulted in high glass transition temperature materials, which were no longer elastomeric. Consequently, the functionalized butadiene monomer was copolymerized with 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene, which has a T_g below room temperature. The resulting polymers were characterized by ^{1}H NMR, ^{13}C NMR, GPC, DSC and TGA measurements.

Chapter 2 describes the synthesis of the alkoxyamine initiator and the synthesis and controlled free radical polymerization of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene using this initiator. The resulting polymers were characterized by ^{1}H NMR, ^{13}C NMR, GPC, DSC and TGA measurements.

CHAPTER 1. SYNTHESIS AND FREE RADICAL POLYMERIZATION OF 2,3-BIS(CYANOPROPYL)-1,3-BUTADIENE

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Abstract

The homopolymerization of 2,3-bis(cyanopropyl)-1,3-butadiene (CPBD) and copolymerization of CPBD with styrene and 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (EOBD) were studied. CPBD homopolymerization produced materials with $<M_n>$ values of 16 x 10^3g/mol and polydispersities ranging from 1.59 to 2.36 in one to two hours. The polymers exhibited solvent resistance to common nonpolar solvents such as hexanes, ethyl ether and benzene. At six hours the resulting polymer was crosslinked and insoluble. Solution copolymerizations of CPBD with styrene or EOBD resulted in materials with $<M_n>$ values of 11 x 10^3 g/mol to 26 x 10^3 g/mol. The glass transition temperatures increased from 23 to 78 °C as styrene incorporation increased from 5-79% and decreased from 16 to –24 °C as EOBD incorporation increased from 8-88%. The reactivity ratios of CPBD and styrene of 2.2 and 0.35 and CPBD and EOBD of 1.29 and 0.26 indicated that the dicyano monomer was more reactive than styrene or EOBD.

Introduction

Functionalized materials have been explored extensively in the literature due to the possibility of introducing the properties of a functional group into high molecular weight materials.[1] Despite the large number of potential applications for functionalized diene-based materials, the attention has been largely directed at styrene-based materials.[2] This lack of research on functionalized butadienes is probably due to the difficulty in synthesizing new diene-based monomers. However, some groups have successfully overcome these difficulties to synthesize functionalized butadienes. Stadler's group reported the synthesis and copolymerization of *N,N*-dialkylaminoisoprenes with styrene and 1,3-butadiene while Penelle's group worked with several siloxy-butadiene derivatives.[3-7] Their work was primarily focused on the anionic polymerization of these monomers.

Our group is mainly interested in the functionalization of 1,3-butadienes using polar groups such as cyano, ester and a variety of amines.[8-12] By utilizing a functionalized monomer, we avoid some of the drawbacks of chemical modification of polymers including side reactions during modification and non-uniformity of functionalization. We have taken our functionalized monomers a step further by synthesizing disubstituted 1,3-butadienes.[10] It is through the incorporation of a disubstituted monomer that the functionality can be doubled within a given repeat unit. In this paper, the disubstituted functionalized 1,3-butadiene synthesized is 2,3-bis(cyanopropyl)-1,3-butadiene (CPBD), which is shown below. The specific functional group was chosen in order to investigate the polar effects of the cyano group on the monomer reactivity and on the polymer's final properties. It is also anticipated that incorporation of the polar monomer as a covalently bound modifier in diene-based materials will aid in crosslinking or in tailoring existing properties. For example, in nitrile rubber (NBR), as the acrylonitrile content increases, the resistance to hydrocarbons, impermeability to gases and thermal resistance increase, but the resilience, the low temperature flexibility and the solution viscosity decrease.[13,14] This indicates that the oil resistance and low temperature flexibility are mutually incompatible. By incorporating the cyano functionalized monomer into NBR or styrene-butadiene rubber (SBR), a solution to this problem could be possible by adding the solvent resistance and oil resistance properties of the cyano group without decreasing the flexibility of the copolymer. It is also anticipated that the cyano group can be derivatized to other functional groups, thus increasing the number of functionalized polymers that could be synthesized. Due to the wide range of properties that CPBD could bring to polymers, materials made with it could have potential applications as additives to improve the compatibilities and mechanical properties of polymer blends, as well as adhesives, packagings and coatings.

In this paper, we report the synthesis of 2,3-bis(cyanopropyl)-1,3-butadiene in a three step synthesis. Our initial work with this monomer has been in the free radical polymerization and copolymerization with styrene and 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (EOBD). The comonomers were chosen due to the potential applications mentioned above.

2,3-bis(cyanopropyl)-1,3-butadiene (CPBD)

Experimental

Materials. All reagents were purchased from Aldrich and used as received unless otherwise reported. Styrene, benzene, tetrahydrofuran and 1,4-dichloro-2-butyne were distilled prior to use. 2,3-Bis(cyanopropyl)-1,3-butadiene was purified by flash chromatography until the ^1H NMR spectrum corresponded to the expected structure and the GCMS showed > 99% purity. AIBN (2,2'-azobisisobutyronitrile) was recrystallized from methanol.

General Characterization. ^1H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ on a VXR-300 at 300 MHz and 75.5 MHz, respectively. A Varian GC fitted with a Finnigan Mat Magnum mass spectrometer was used for product identification. High-resolution mass spectrometry was performed with a Kratos MS50TC at a resolution (*R*) of 14,300 in electron impact (EI) mode with an electron beam energy of 70 eV. Polymer ^{13}C NMR spectra were determined in $CDCl_3$ on a XR-200. Molecular weights of the polymers were determined with a Wyatt gel permeation chromatograph using polystyrene standards and tetrahydrofuran (THF) unless otherwise stated using chloroform. The glass transition temperatures (T_g) were determined with a Perkin-Elmer Pyris differential scanning calorimeter (DSC) at a heating rate of 10 °C per minute from –75 °C to 150 °C with a nitrogen purge. Glass transition temperatures were reported on the basis of the second heating. Weight loss was determined using Perkin-Elmer Pyris thermal gravimetric analysis (TGA) at a heating rate of 10 °C per minute from 30 °C to 450 °C under nitrogen or air.

Synthetic Procedures

Synthesis of 2,3-Bis(cyanopropyl)-1,3-butadiene.

4-Iodobutyronitrile. Acetone (700 mL) and sodium iodide (90 g, 600 mmol) were added to a one-necked, 1.0 L round-bottom flask, equipped with a water condenser. 4-Chlorobutyronitrile (7.9 mL, 110 mmol) was then added and the mixture was refluxed for 12 hours. The solution was cooled and concentrated using a rotary evaporator. Approximately 100 mL of water were added to dissolve the salt. The aqueous layer was extracted twice with diethyl ether (150 mL), washed with brine, dried over magnesium sulfate and filtered. The extracts were concentrated and distilled over copper powder under reduced pressure to provide the liquid product. ^{1}H NMR, ($CDCl_3$): δ 2.14 (p, 2H; *J* = 9 Hz, -C$\underline{H}_2$), 2.55 (t, 2H; *J* = 9 Hz, -C$\underline{H}_2$CN), 3.33(t, 2H; *J* = 9 Hz, -C$\underline{H}_2$I). ^{13}C NMR, ($CDCl_3$): 3.5 (-$\underline{C}H_2$), 17 (-$\underline{C}H_2$-CN), 29 (-$\underline{C}H_2$I), 118 (-$\underline{C}$N).

2,3-Bis(cyanopropyl)-1,3-butadiene.[15,16] Zinc granules (30 mesh, 39 g, 600 mmol) and 120 mL of THF were added to a flame-dried argon-purged three-necked, 250 mL round-bottom flask. Over one hour, 12 mL of 1,2-dibromoethane was added, while refluxing, to activate the zinc. 4-Iodobutyronitrile (39 g, 200 mmol) was added and stirred at 50 °C for 24 h then cooled to room temperature. Lithium chloride (17 g, 400 mmol) was added to a two-necked, 500 mL round-bottom flask. The flask was evacuated and flame dried several times to remove any excess water from the salt and from the surface. After purging with argon, copper cyanide (18 g, 200 mmol) was added to the flask under a strong flow of argon. The flask was then evacuated and purged with argon three times. After the addition of THF (200 mL), the solution was cooled to –30 °C. The 4-iodobutyronitrile solution was added via cannula to the cold solution. The solution was then warmed to 0 °C, held at that temperature for 10 minutes and cooled to –78 °C. This was followed by the dropwise addition of 1,4-dichloro-2-butyne (4.4 mL, 45 mmol). The solution was stirred for 12 hours as it warmed to room temperature. The flask was opened and its contents were poured into a saturated ammonium chloride solution to quench any residual cuprate. The aqueous layer was extracted twice with 150 mL of diethyl ether, washed with brine and finally washed with sodium thiosulfate in order to remove any iodine from the solution. The organic layer was dried over magnesium sulfate, filtered and concentrated under vacuum to provide a crude oil. The product was purified by filtration by passing through a basic alumina column followed by a silica gel column (5% ethyl acetate in hexanes mixture gradually increasing to a 15% ethyl acetate in hexanes mixture) to produce 5.1 g (27 mmol) of 2,3-bis(cyanopropyl)-1,3-butadiene in 61% yield and > 99% purity by GC-MS. ^{1}H NMR, ($CDCl_3$): δ 1.81 (p, 4H; J = 7.3 Hz, -C$\underline{H}_2$-C-CN), 2.34 (t, 4H; J = 7.1 Hz, -C$\underline{H}_2$-CH$_2$), 2.41 (t, 4H; J = 7.5 Hz, -C$\underline{H}_2$CN), 5.94 (d, 2H; J = 0.6 Hz, -CH=), 5.15 (d, 2H; J = 0.6 Hz, -CH=). ^{13}C NMR, ($CDCl_3$): δ 17 (-$\underline{C}$H$_2$-C-CN), 24 (-$\underline{C}$-CN), 33 (-$\underline{C}$H$_2$-C), 114 (-CH=), 120 (CN), 145 (-C=). High-resolution mass spectrometry: theoretical mass 188.13135, measured mass 180.98882, deviation 1.4 ppm.

Homopolymer Synthesis.

Bulk and solution polymerization of 2,3-bis(cyanopropyl)-1,3-butadiene. One gram of 2,3-bis(cyanopropyl)-1,3-butadiene, 0.5 mole % 2,2'-azobisisobutyronitrile (AIBN), 1 mL ofsolvent (for solution polymerizations only) and a stir bar were added to an ampoule. After three freeze-pump-thaw cycles, the ampoules were sealed under vacuum and then allowed to warm to room temperature before being placed in a constant temperature oil bath for the allotted time. The ampoules were broken and the reaction was inhibited with 5 mg 2,6-di-*tert*-butyl-4-methyl-phenol (BHT). The polymer was precipitated twice from dichloromethane into methanol. The polymer was dried under vacuum and then analyzed. ^{1}H NMR, ($CDCl_3$): δ 1.6 (m, 4H; -C$\underline{H}_2$-C-CN), 2.05 (t, 4H; C$\underline{H}_2$-C=), 2.2 (t, 4H; -C$\underline{H}_2$-C=), 2.4 (d, 4H; -C$\underline{H}_2$CN). ^{13}C NMR, ($CDCl_3$): δ 17.3 (-$\underline{C}H_2$-C-CN), 24.9 ($\underline{C}H_2$-CN), 30.6 (-$\underline{C}H_2$-C=), 114.2 (-CH=), 120.1 (CN), 133.5 (-C=). Elemental analysis: 75.87% C, 9.08% H and 14.52% N.

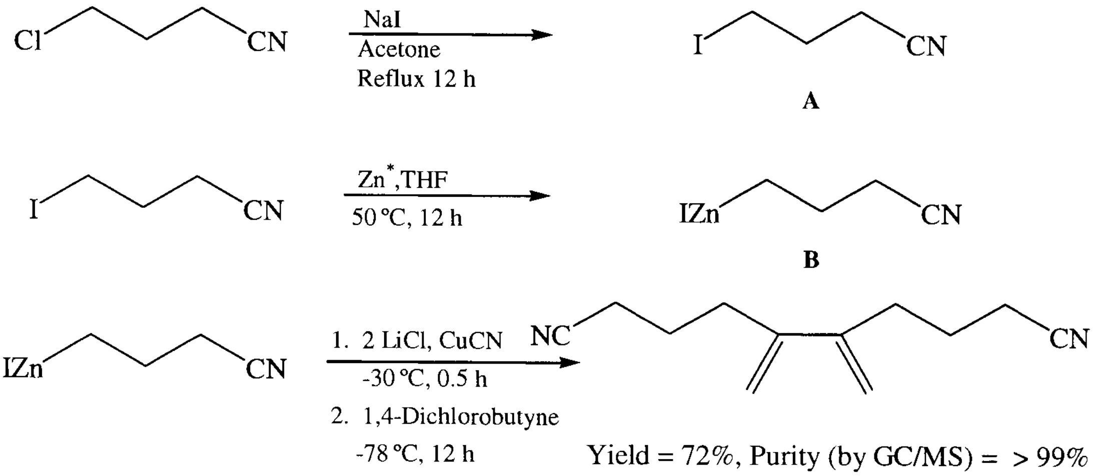
Copolymer Synthesis.

General procedure for solution copolymerization. One gram of 2,3-bis(cyanopropyl)-1,3-butadiene, 0.5 mole % AIBN and a stir bar were added to an ampoule. The required amount of styrene or 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene was added according to the feed ratio and benzene was added on a one to one ratio by volume. After three freeze-pump-thaw cycles, the ampoules were sealed under vacuum and then allowed to warm to room temperature before being placed in a constant temperature bath for the allotted time. The ampoules were broken and the reaction was inhibited with 5 mg of BHT. The polymer was precipitated twice from dichloromethane into methanol. The polymer was dried under vacuum and then analyzed. Poly(CPBD-*co*-styrene): ^{1}H NMR, ($CDCl_3$): δ 1.5 (m, 2H; -C$\underline{H}_2$-C-Ph), 1.6 (m, 4H; -C$\underline{H}_2$-C-CN), 1.8 (m, 1H; -C$\underline{H}$-Ph) , 2.05 (t, 4H; C$\underline{H}_2$-C=), 2.2 (t, 4H; -C$\underline{H}_2$-C=), 2.4 (d, 4H; -C$\underline{H}_2$CN), 6.5-7.2 (6H, aromatic). ^{13}C NMR: 17.3 (-$\underline{C}H_2$-C-CN), 24.7 (CH-Ph), 24.9 ($\underline{C}H_2$-CN), 30.6 (-$\underline{C}H_2$-C=), 114.2 (-$\underline{C}$H=), 120.1 (CN), 133.5 (-C=), 126.6, 128.0, 128.5, 134.5 and 144.4 (aromatic). Poly(CPBD-*co*-EOBD): ^{1}H NMR, ($CDCl_3$): δ 1.25 (t, 6H; CH_3), 1.6 (m, 4H; -C$\underline{H}_2$-C-CN), 1.68 (m, 4H; -C$\underline{H}_2$), 2.05 (t, 4H;

$C\underline{H}_2$-C= and t, 4H, -$C\underline{H}_2$-CO_2), 2.09 (t, 4H, -$C\underline{H}_2$-C=), 2.2 (t, 4H; -$C\underline{H}_2$-C=), 2.29 (t, 4H, -$C\underline{H}_2$-C=), 2.4 (d, 4H; -$C\underline{H}_2CN$), 4.12 (q, 4H; -$OC\underline{H}_2$). ^{13}C NMR ($CDCl_3$): δ 14 (-$\underline{C}H_3$), 17.3 (-$\underline{C}H_2$-C-CN), 24.9 ($\underline{C}H_2$-CN), 30.6 (-$\underline{C}H_2$-C=), 31 (-$\underline{C}H_2$-CO_2), 31.5 (-$\underline{C}H_2C$=), 34 (-$\underline{C}H_2$-C=), 60 (-$O\underline{C}H_2$), 114.2 (-$\underline{C}H$=), 120.1 (CN), 133 (-C=C), 133.5 (-C=), 174 (-CO_2).

RESULTS AND DISCUSSION

Monomer Synthesis. The three-step synthesis of CPBD is a versatile synthetic method that can be used to produce a number of disubstituted 1,3-butadienes, shown in Scheme 1. The S_N2' reaction with 1,4-dichlorobutyne provides an efficient process by which the disubstituted 1,3-butadienes can be formed. By using a wide variety of cuprates, this process allows for different functionalities to be added to the butadiene in high yield and high purity. The resulting CPBD is reactive and must be kept at a temperature lower than 0 °C in order to avoid unwanted polymerization. The first step in the synthesis is an S_N2 reaction on 4-chlorobutyronitrile to form 4-iodobutyronitrile (A). The halogen exchange was used to provide the next step with higher reactivity starting material. The zinc powder in THF was activated by the addition of 1,2-dibromoethane (DBE) and subsequently 4-iodobutyronitrile was added to form the zinc inserted product (B). The next step led to a copper complex with the iodozinc compound by the addition of copper cyanide and lithium chloride. Once the copper complex was formed, the final product was made by the addition of 1,4-dichlorobutyne to initiate the S_N2' insertion. The final product was purified by column chromatography resulting in an overall yield of 72%. The monomer was characterized by ^1H NMR and ^{13}C NMR and was found to be greater than 99% pure by GC/MS. High resolution mass spectrometry also verified that CPBD had a deviation of 1.4 ppm. The monomer is



Scheme 1. Synthesis of 2,3-bis(cyanopropyl)-1,3-butadiene (CPBD).

easily purified by column chromatography, thus we have been able to overcome the difficulty in synthesizing new functionalized 1

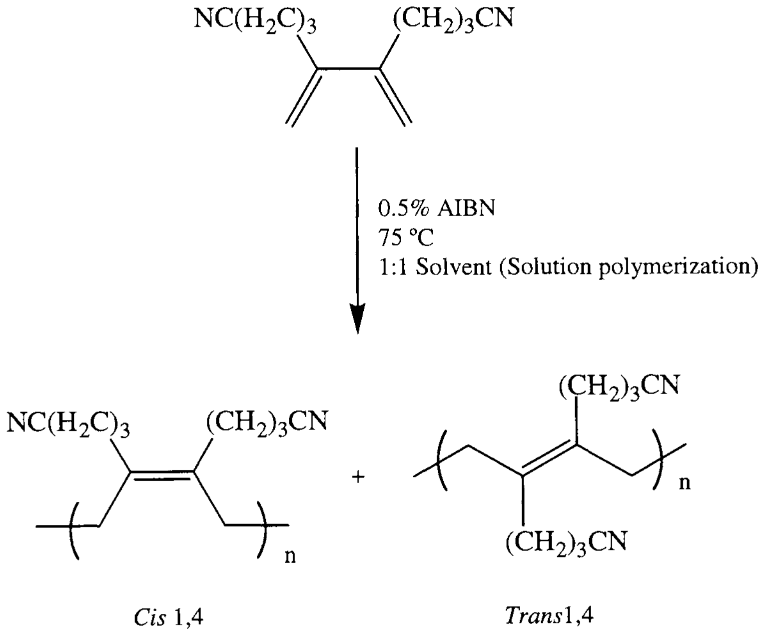
Homopolymer Synthesis. Bulk and solution free radical polymerization methods were used to synthesize poly(CPBD), as shown in Scheme 2. The results of these polymerizations performed at 75 °C and 0.5 mole % are shown in Table 1. The 75 °C temperature was chosen based on the ten hour half-life associated with AIBN. Bulk free radical polymerization resulted in materials with moderate molecular weights (8.6 x 10^3 g/mol and 15.5 x 10^3g/mol), polydispersities of 1.59 and 2.36 and low yields (9% and 14%) for one and two hours, respectively. Crosslinked material was produced after 6 hours. Several limitations are evident from the homopolymerization of CPBD: the polymer's polydispersity index (PDI) increases from 1.59 to 2.36 when the time is increased from one hour to two hours and the polymer is easily crosslinked. Thus the control of this polymerization is problematic. The solution polymerizations in acetonitrile and benzene also resulted in moderate molecular weight materials (13.8 x 10^3g/mol and 10.2 x 10^3 g/mol) and polydispersities of 1.49 and 1.52 respectively, with some precipitation occurring in benzene.

The thermal gravimetric analysis (TGA) data for all uncrosslinked homopolymers showed a five percent weight loss of 337 ± 5 °C and 330 ± 5 °C under nitrogen and air, respectively (Table 2). The glass transition temperature (T_g) of these homopolymers was found to be 13 ± 3 °C. This is higher than our other functionalized diene based materials such as poly(2,3-bis(-4-ethoxy-4-oxobutyl)-1,3-butadiene) (Tg = -37 °C), poly(2-cyanomethyl-1,3-butadiene) (Tg = - 18 °C) and poly(2-[(*N*-benzyl-*N*-methylamino)methyl]-1,3-butadiene (-14 °C) .[8,10,12] Since the T_g is close to room temperature, the material when crosslinked is likely to be less flexible decreasing the elastomeric properties runs.

The uncrosslinked homopolymer was insoluble in many nonpolar solvents such as ethyl ether, benzene and hexanes, as well as being insoluble in methanol. The homopolymer also exhibited decreased solubility in tetrahydrofuran (THF), which had a solubility of 0.33 g/L as seen in Table 3. The solvent resistance causes a number of characterization difficulties such as decreasing the number of viable solvents for gel permeation chromatography (GPC). The ^{1}H NMR (Figure 1) of the polymer shows that all materials contained (as shown by the absence of peaks in the region of 5-7 ppm) 1,4-microstructure. The 1,4-microstructure is believed to be a result of the steric bulk around the two and three positions of butadiene. Despite the benefits of solvent resistance and relatively short polymerization times, these properties cause difficulties in characterization and processing of the polymers.

As a result of these limitations, the copolymerizations of CPBD are more interesting. Through the copolymerization it was determined that many of the limitations are lessened or eliminated completely. Upon copolymerization of CPBD, the solvent resistance that caused characterization difficulties in the homopolymers is decreased, the monomers are able to polymerize for longer times without crosslinking and the yields are increased. When CPBD is copolymerized with EOBD the glass transition temperatures are decreased. EOBD was chosen for copolymerization with CPBD because of its low T_g as well as functionality. It is anticipated that by combining CPBD with EOBD, the resulting material will combine the solvent resistance of CPBD with the flexibility and processability of EOBD.

Copolymerization of 2,3-Bis(cyanopropyl)-1,3-butadiene. The first copolymers (6-10, shown in Table 4) were synthesized from CPBD and styrene in order to make a material similar in structure to styrene-butadiene rubber (SBR) (Scheme 3). SBR is made by emulsion polymerization and consists of 25% styrene and 75% butadiene. The properties of SBR are limited to properties associated with these two monomers. By copolymerizing the functionalized butadiene monomer with styrene, a functionalized SBR was made. It was



Scheme 2. Bulk and solution free radical polymerization of CPBD.

Table 1. Homopolymerization of CPBD.

Entry #	Time h	Solvent 1:1 Volume Ratio	$\langle M_n \rangle^a$ x 10^{-3} g/mol	$\langle M_w \rangle^a$ x 10^{-3} g/mol	PDI[a]	Conv. wt. %	GPC G#
1	1.0	NA	15.5	24.6	1.59	9	**G1**
2	2.0	NA	8.6	20.2	2.36	14	**G2**
3	6.0	NA	c	-	-	-	-
4	24	Acetonitrile	13.8	20.5	1.49	38	**G3**
5	24	Benzene[b]	10.2	15.4	1.52	37	**G4**

[a] run in $CHCl_3$, by GPC based upon poly(methyl methacrylate) standards, samples 1 mg/mL
[b] some precipitation occurred
[c] crosslinked, insoluble

Table 2. Thermal data for the homopolymerization of CPBD.

Entry #	T_g °C	Weight Loss Nitrogen °C		Weight Loss Air °C	
		5%	10%	5%	10%
1	15	338	356	333	348
2	13	336	353	328	349
4	13	337	357	335	357
5	10	335	358	330	351

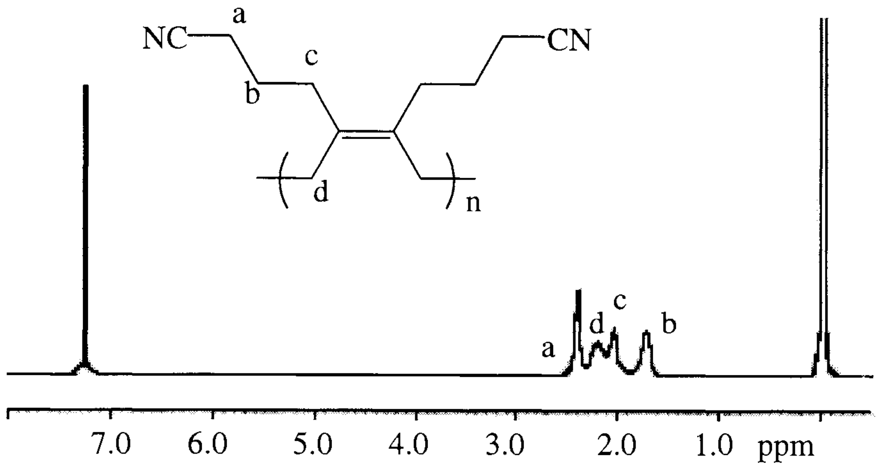


Figure 1. ^{1}H NMR spectrum of Poly(CPBD).

Table 3. Solubility of poly(CPBD).*

Solvent	Solubility (g/L)
Hexanes	0
Methanol	0
Benzene	0
Ethyl Ether	0
Tetrahydrofuran	0.33
Acetonitrile	≥ 1
Acetone	≥ 1
Methylene Chloride	≥ 1
Chloroform	≥ 1

* Conditions: polymers were stirred for 24 h at 500 rpms in solvent at a concentration of 1 mg/mL. Then the solvent was poured off, the remaining polymer was dried under vacuum for 24 h and weighed.

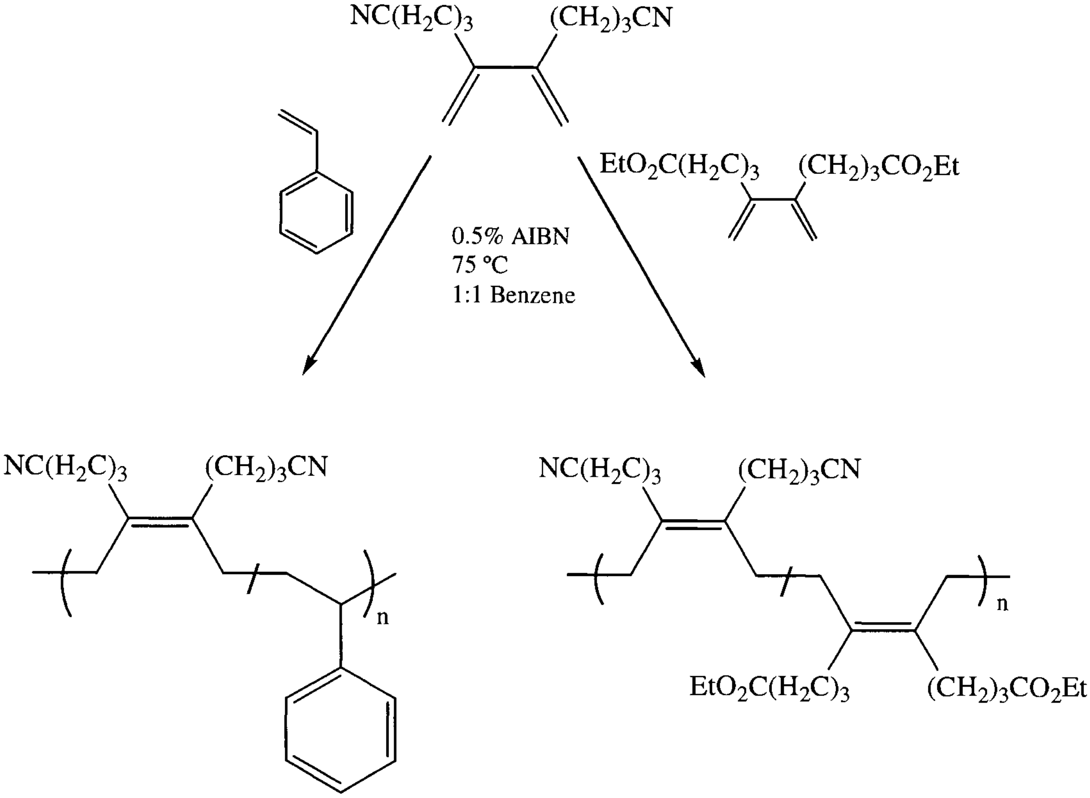
anticipated that the resulting materials would have added properties from the nonfunctionalized SBR such as increased solvent resistance. The results of the copolymerization are shown in Table 4. As can be seen, when the CPBD feed composition increased from 10% to 90%, the copolymer composition increased in CPBD from 21% to 95% in 24 hours. The incorporation of CPBD is always higher than the feed. This behavior is consistent with the reactivity ratios of the pair of monomers, which will be discussed later. The $<M_n>$ values range from 15.5 x 10^3 g/mole to 31.5 x 10^3 g/mole and the PDIs range from 1.49 to 1.64. These molecular weights are close to the number-average molecular weights obtained during homopolymerization under the same conditions. The conversion of copolymers 6-10 increases from 30 to 72%. The conversion increase can be explained by the apparent decreased rate of polymerization of the functionalized butadiene over styrene.

The ^1H NMR spectra (300 MHz, $CDCl_2$) of copolymers 6-10 are shown in Figure 2. The peaks could be assigned by comparison with the ^1H NMR of polystyrene (PS) and poly(CPBD) homopolymers. The aromatic regions (7.0-7.3 ppm) were attributed to the phenyl group of the styrene repeat unit. The peaks associated with the aliphatic region of PS overlap with those of poly(CPBD). Thus, the styrene aliphatic hydrogens were subtracted from the total aliphatic region, which allowed for the calculation of the incorporation ratio of CPBD to styrene. The ^1H NMR clearly shows that as the feed ratio of CPBD decreases, the incorporation of CPBD decreases. In all cases, no obvious 1,4-microstructure was seen.

The copolymerization of CPBD and styrene resulted in glassy materials. In order to maintain the material's elastomeric properties, the polymer must have a glass transition below room temperature. Therefore, CPBD was copolymerized with EOBD (T_g = –37 °C) to lower the glass transition temperatures of the polymers. EOBD was also chosen for its ease of derivatization and functionality which can then further adjust the material's properties. The series of copolymerizations combining CPBD and EOBD (11-15) were synthesized in THF and their results are shown in Table 5. As can be seen, when the feed composition of CPBD increased, the incorporation composition also increased. Similar to the poly(2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene), the CPBD composition was always higher than the EOBD composition. However, the differences were not as great as those observed in the copolymerization with styrene. These materials are in a similar molecular weight range as those found in the previous copolymer system. These molecular weights range from 11.4 x 10^3 g/mol to 25.5 x 10^3 g/mol as shown in Table 6. The polydispersities range from 1.33 to 1.56 with the PDIs < 1.5 attributed to the loss of low molecular weight material during work-up.

The ^{1}H NMR spectra (300 MHz, CD_2Cl_2) of the copolymers 11-15 are shown in Figure 3. The peaks could be assigned by comparison with the ^{1}H NMR of poly(EOBD) and poly(CPBD). The peaks at 1.25 and 4.1 were attributed to the hydrogens on the ethyl group of the ester. The methylene peaks from both poly(CPBD) and poly(EOBD) overlap (1.5-which allowed for the calculation of the incorporation ratio of CPBD to EOBD. ^{1}H NMR clearly shows that as the feed ratio of CPBD decreases, the incorporation also decreases.

Reactivity Ratios. The composition of a copolymer is dependent upon the concentration of the monomers and the reactivity of the monomers relative to the propagating chain ends, thus it is imperative to determine the reactivity ratios of the monomers in a copolymerization system. There are two methods that have been used to calculate the reactivity ratios of comonomers in the literature.[17,18] The first method is based on the



Scheme 3. Solution copolymerization of CPBD with styrene and 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (EOBD).

Table 4. Solution copolymerization of styrene and CPBD.

Entry #	Feed % CPBD	$\langle M_n \rangle^a$ x 10^{-3} g/mol	$\langle M_w \rangle^a$ x 10^{-3} g/mol	PDI[a]	Inc.[b] % CPBD	Conv. wt. %	GPC G#
6	90	15.5	23.2	1.49	95	30	**G5**
7	75	18.0	27.2	1.51	85	45	**G6**
8	50	31.5	51.5	1.63	65	47	**G7**
9	25	26.4	42.4	1.61	45	65	**G8**
10	10	25.5	41.9	1.64	21	72	**G9**

[a] run in THF, by GPC based upon polystyrene standards
[b] calculated by ^{1}H NMR

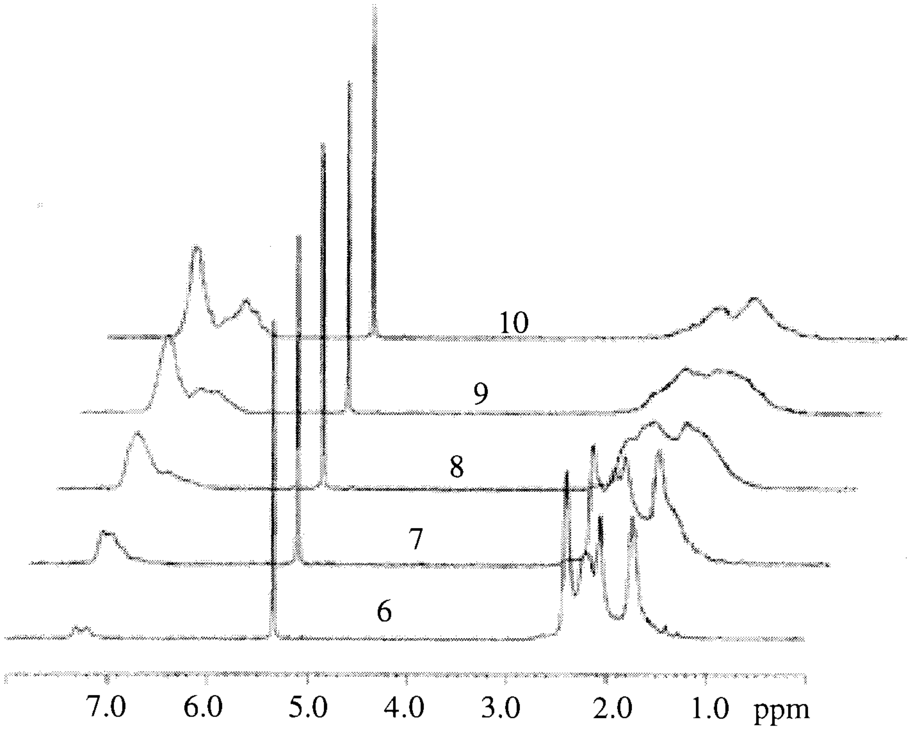


Figure 2. ^{1}H NMR spectra of copolymers 6-10 in CD_2Cl_2.

Table 5. Solution copolymerization of EOBD and CPBD.

Entry #	Feed % CPBD	$\langle M_n\rangle^a$ x 10^{-3} g/mol	$\langle M_w\rangle^a$ x 10^{-3} g/mol	PDI[a]	Inc.[b] % CPBD	Conv. wt. %	GPC G#
11	90	16.8	24.9	1.48	92	24	**G10**
12	75	17.5	25.3	1.45	81	30	**G11**
13	50	22.6	31.7	1.40	62	15	**G12**
14	25	11.4	17.9	1.56	33	24	**G13**
15	10	25.5	33.9	1.33	12	11	**G14**

[a] run in THF, by GPC based upon polystyrene standards
[b] calculated by ^{1}H NMR

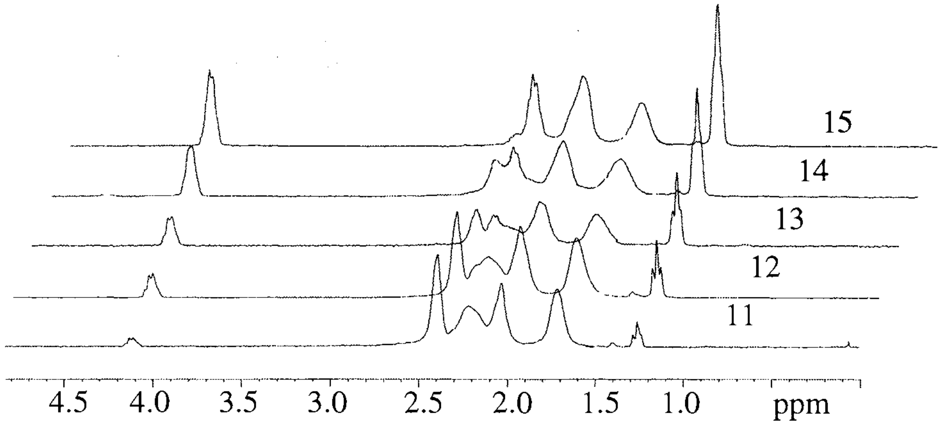


Figure 3. ^{1}H NMR spectra of copolymers 11-15 in CD_2Cl_2.

copolymer composition and conversion. The second method uses information obtained from monomer sequencing. Since it is difficult to determine a monomer sequence by NMR, this method is seldom used.

We have chosen to use NMR techniques combined with the first method and the Mayo-Lewis equation to determine the reactivity ratios. This equation allows for conversions higher than 10%, unlike the traditional calculations that require conversions lower than 5%.[17,18] Upon plotting the reactivity ratios of these two monomers, the r values can be approximated to $r_1 = 2.2 \pm 0.1$ and $r_2 = 0.35 \pm 0.05$ for CPBD and styrene, respectively (Figure 4). For the best results the lines should cross at one point, but in this graph the result is a narrow range in which the actual ratios are located. One of the reasons for this inaccuracy could be the higher monomer to polymer conversions, however, there is also a higher instrumental error associated with determining the reactivity ratios from NMR

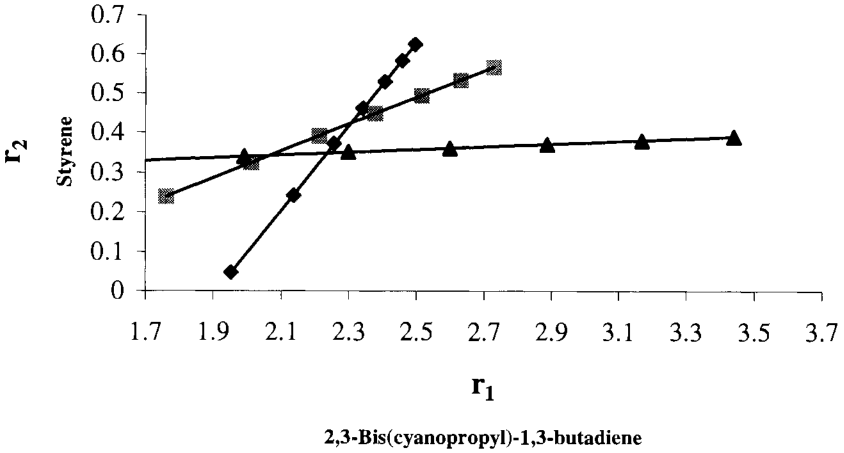


Figure 4. Reactivity ratios of CPBD and styrene.

than other methods such as gas chromatography, which requires very low conversions (< 10%).

The same method was used to determine the reactivity ratios of CPBD and EOBD. Upon plotting the reactivity ratios of these two monomers, the r values are shown to be r_1 = 1.29 and r_2 = 0.26 for CPBD and EOBD, respectively (Figure 5). This method shows very good accuracy in determining the reactivity ratios, which is shown by the lines all intersecting at one point. The calculated reactivity ratios for both copolymerizations are consistent with the observed incorporation data in which CPBD incorporated preferentially to styrene and EOBD, thus the copolymer will always be richer in CPBD than styrene or EOBD. However, r_1 was greater in the copolymerization with styrene than with EOBD. This indicates that there is a propensity for the functionalized butadienes to homopropagate rather than cross propagate.

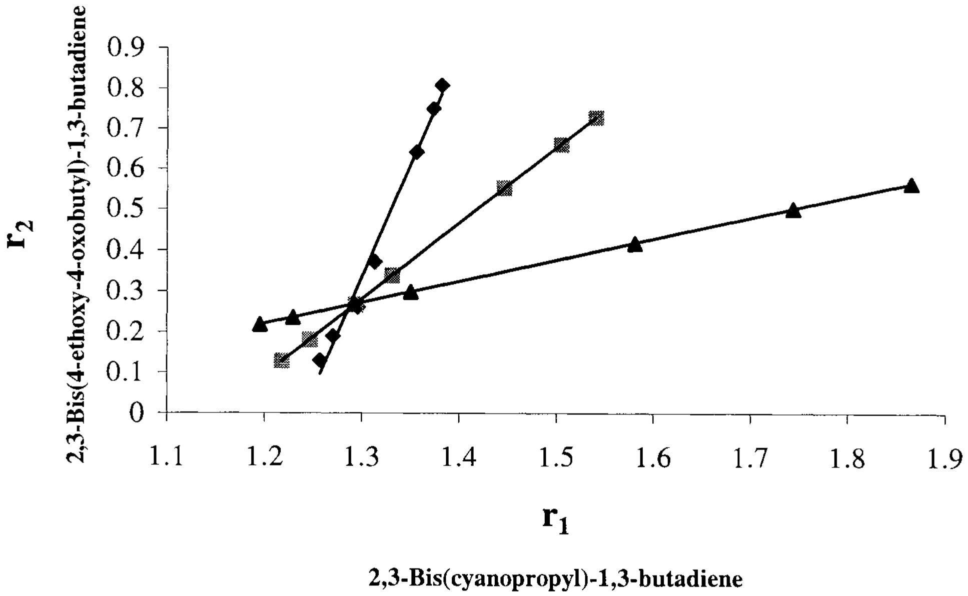


Figure 5. Reactivity ratios of CPBD and EOBD.

Thermal Properties. The thermal properties of copolymers 6-10 (CPBD incorporation decreasing from 95 to 21%) are shown in Table 6. The thermal gravimetric analysis (TGA) shows a small increase as the CPBD incorporation decreases (346 to 325 °C and 340 to 319 °C in nitrogen and air, respectively) for the 5% weight loss. The increase in the thermal stability of the copolymer with increasing CPBD incorporation may be due to the increase in nitrile groups; thus increasing the polar interactions between the molecules. While there is a small increase in the TGA values of copolymers 6-10, copolymers 11-15 exhibit larger increases from 248 to 341 °C and from 234 to 339 °C for the 5% weight loss in nitrogen and air, respectively, with increasing CPBD incorporation (Table 7). This could be due to styrene having a less detrimental effect on the thermal stability because the benzene ring is more stable.

Also shown in Tables 6 and 7 are the glass transition temperatures (T_g) of copolymers 6-15. As the feed ratio of CPBD is decreased in copolymers 6-10, the T_g increases from 23 to 78 °C. All the materials made from CPBD and styrene are glassy and therefore cannot be used as a rubber. For copolymers 11-15, as the feed ratio of CPBD is decreased, the T_g decreases from 16 to –24 °C. With the decrease in glass transition temperature, the materials synthesized are rubbery and thus have potential applications in the adhesive, packagings and coatings industry. Each copolymer has only one T_g indicating that the polymer is random rather than block in structure. Figures 6 and 7 illustrate the dependence of the T_g on the incorporation of CPBD, whereby the theoretical values of the T_g were calculated using Equation 1. The Gordon-Taylor equation ($k = 0.6$, W_1 = weight percent of CPBD incorporated, W_2 = weight percent of styrene or EOBD incorporated) has been shown to be useful in calculating theoretical glass transition temperatures for other butadiene and styrene copolymers because of its versatility for comonomers that have significantly different glass transition temperatures. There is a good correlation between the experimental and the theoretical T_g as the theoretical line generally falls within the error bars of the experimental and follows the same trends as the experimental for each copolymer series.

$$T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) \qquad \text{Equation 1}$$

Table 6. Thermal data for the solution copolymerization of styrene and CPBD.

Entry #	T_g °C	Weight Loss Nitrogen °C		Weight Loss Air °C	
		5%	10%	5%	10%
6	23	346	362	340	359
7	37	341	359	336	355
8	48	347	361	337	354
9	66	329	351	325	351
10	78	325	357	319	351

Table 7. Thermal data for the solution copolymerization of CPBD and EOBD.

Entry #	T_g °C	Weight Loss Nitrogen °C		Weight Loss Air °C	
		5%	10%	5%	10%
11	16	341	360	339	354
12	12	335	352	333	351
13	-6	261	304	270	315
14	-16	275	311	246	292
15	-24	248	282	234	264

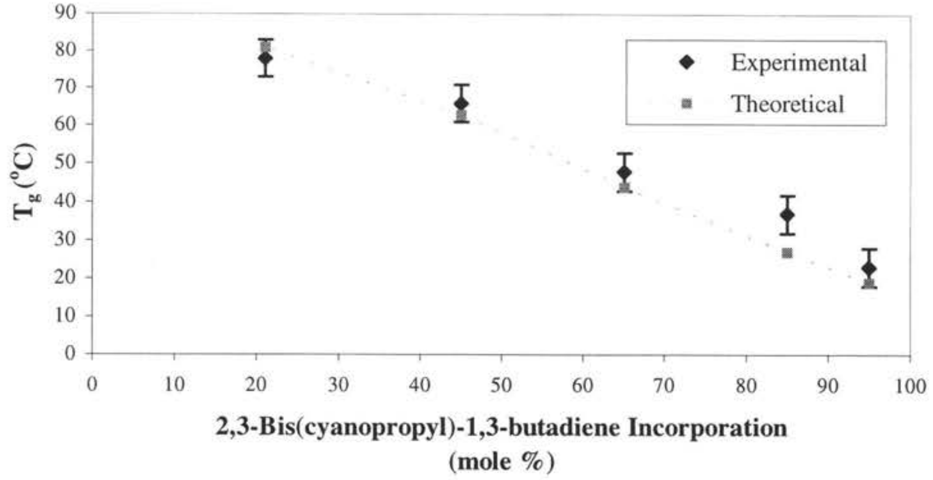


Figure 6. Graph of experimental versus theoretical glass transition temperatures calculated by the Gordon-Taylor equation for the copolymerization of CPBD with styrene.

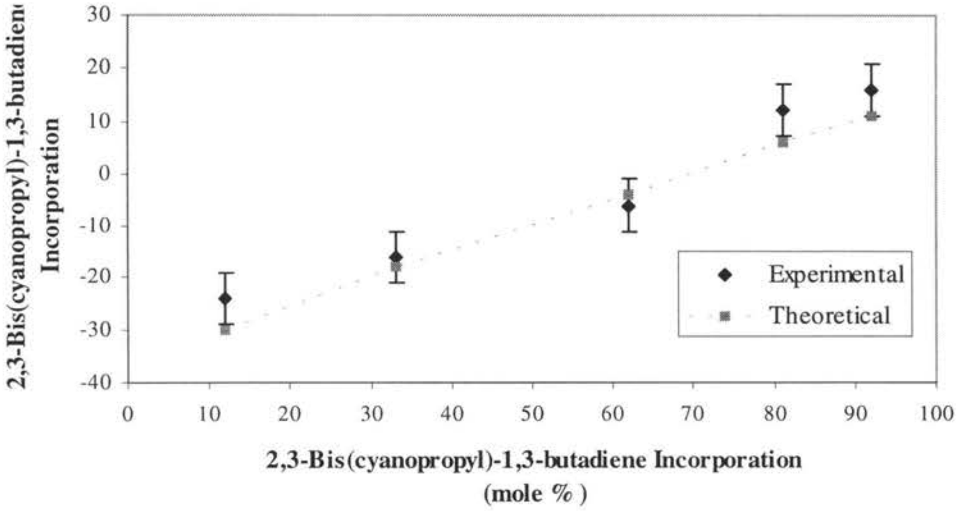


Figure 7. Graph of experimental versus theoretical glass transition temperatures calculated by the Gordon-Taylor equation for the copolymerization of CPBD and EOBD.

CONCLUSIONS

Poly[2,3-bis(cyanopropyl)-1,3-butadiene], poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] and poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] have been successfully polymerized via free radical bulk and solution polymerization, and the copolymerization behavior was investigated. The reactivity ratios of CPBD with styrene and EOBD were determined by the Mayo-Lewis equation. The cyano-substituted monomer had a higher reactivity than styrene and EOBD. The resulting copolymers' glass transition temperatures were dependent on the copolymer composition and fit the Gordon-Taylor equation. All the copolymers obtained were random, noncrystalline polymers, which showed only one T_g on DSC.

Although this paper focuses on the copolymerization of CPBD with one other monomer, the potential to utilize CPBD as a third monomer in commercial materials, such as SBR and NBR is evident. The high reactivity of CPBD should allow it to add readily to such materials. In addition to the high reactivity, the cyano group's good solvent resistance and thermal stability should lend new properties to the resulting materials while maintaining the flexibility of the rubber. These properties combined into the elastomers should extend the potential applications of these materials to include adhesives, packagings and coatings. the potential applications of this material to include adhesives, packagings and coatings.

ACKNOWLEDGEMENT

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CHAPTER 2. CONTROLLED FREE RADICAL POLYMERIZATION OF 2,3-BIS(4-ETHOXY-4-OXOBUTYL)-1,3-BUTADIENE

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Abstract

The nitroxide mediated free radical polymerization of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (EOBD) was studied. Using 1.0 mole % free nitroxide, the conversions increased from 18 to 53% with increasing time (12 to 36 hours), as expected for a controlled free radical polymerization. After 36 hours the polymerization terminated. Upon addition of 5 mole % free nitroxide, higher conversion (71%) was achieved with 1.0 mole % initiator. However, at lower initiator concentrations of 0.5 and 0.1 mole %, termination was seen at 49 and 20 % conversion, respectively. Decreasing the free nitroxide concentration to 2.5 mole % allowed for greater conversions of 59 and 70 % conversion at 0.5 and 0.1 mole %, respectively. However, for 1.0 mole % initiator the data resembled that from the polymerization with no free nitroxide added, whereby the conversion terminated at 59 % at 24 hours. The molecular weight for these polymerizations ranged from 1.2×10^4 to 3.9×10^4 g/mol. When higher molecular weights were achieved polydispersities increased to as high as 2.37. Under bulk polymerization conditions, conversions as high as 86% were achieved with 2 mole % acetic anhydride with PDIs ranging from 1.31 to 1.97. Further experimentation is needed to gain control of this system.

Introduction

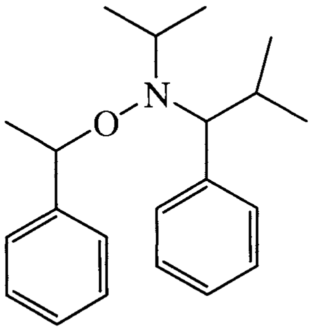
There continues to be significant interest in incorporating functionality into polymeric materials. Through this incorporation, one can tailor a polymer's physical and mechanical properties. Our group has been particularly interested in producing polar functionalized diene-based materials. Functionalities such as amines, nitriles, esters and silyl ethers have already been incorporated onto diene-containing polymer backbones.[1-16] There are two methods that have been used to incorporate such functionality into the polymer backbone. The first method utilizes chemical modification of the existing polymer. However, the uniformity of functional group incorporation cannot be guaranteed. The second method can guarantee uniformity by the polymerization of a functionalized monomer. Our group has investigated a number of substituted dienes with moieties including dialkylamines, nitriles and esters.[5-8,15,16] Previous work on these monomers by our group has included traditional bulk, solution and emulsion free radical studies.

Due to the lack of control of the molecular weight and polydispersities offered by these polymerization techniques, it was necessary to look elsewhere for the desired control. It is anticipated that anionic and nitroxide mediated polymerization will produce controlled molecular weights, low polydispersities (< 1.4) and an extendable chain end for the polymerizations of our functionalized 1,3-butadienes. The extendable chain end will allow us to synthesize block copolymers. Stadler *et al.* anionically polymerized a number of linear, branched and cyclic 2-(*N,N*-dialkylaminomethyl)-1,3-butadienes (dialkylaminoisoprenes) and discovered that bulkier monomers led to more *cis*-1,4 incorporation than the smaller, less bulky amine monomers. In the anionic homopolymerizations, high molecular weight polymers and quantitative conversions were not easily achieved. Quantitative conversions were achieved upon copolymerization with styrene when small concentrations of the aminoisoprenes were used. Beyond the random copolymers, dialkylaminoisoprenes have been incorporated into a triblock copolymer with styrene and *t*-butyl methacrylate, where the *t*-butyl methacrylate was later converted to poly(methacrylic acid) producing triblock coamphilytes.[1-4] Anionic polymerization remains a good option for polymerizing dialkylaminoisoprenes in a controlled fashion, but is limited by functionality.

Our substituted 1,3-butadienes containing polar functionalized groups such as esters and nitriles are not viable options for anionic polymerization. These groups have α-acidic hydrogens to the functional group that could easily be removed, terminating the polymerization. It is for this reason that we chose to explore controlled free radical techniques. There are several controlled free radical techniques that are currently being employed: atom transfer radical procedures (ATRP), 2,2,6,6-tetramethylpiperdinoxy (TEMPO) and other nitroxide mediated polymerizations.[17-19] Despite the number of controlled free radical techniques, only one option is currently feasible for the controlled polymerization of these functionalized monomers. ATRP and TEMPO are limited by the presence of diene monomers; whereas the nitroxide mediated polymerizations described by Hawker are neither limited by the presence of a diene nor the presence of a functional group.

Benoit *et al.* studied a wide variety of alkoxyamines in pursuit of a universal initiator.[19] Their experimentation produced an α-hydrido alkoxyamine (**I**) that when used to polymerize a number of different monomers resulted in polymers with controlled molecular weights, low polydispersities and extendable chain ends. Through the use of this initiator, Benoit *et al.* were able to successfully polymerize diene-based monomers such as isoprene, butadiene and acrylates.[20] Since this nitroxide mediated polymerization can be utilized with diene and functionalized acrylate monomers, we projected that this system would be successful with our functionalized 1,3-butadiene monomers. Prior to this nitroxide mediated system, the block copolymerization of our nitrile and ester monomers was not a possibility. Benoit *et al.* showed that they were able to synthesize random and block copolymers utilizing monomers that were either diene-based or functionalized.[20] The block copolymerization of isoprene and styrene showed greater efficiency and lower polydispersities when styrene was used as the initial block. However, during the block copolymerization of styrene and *t*-butyl acrylate, it was necessary to use the acrylate as the starting block. Incomplete initiation was observed when the polymer was grown in the opposite direction. Through this new nitroxide mediated technique, Benoit *et al.* have expanded the potential applications of functionalized monomers to include those associated with block copolymers.

In this paper the bulk and solution polymerization of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (EOBD) will be discussed. Upon block copolymerization these polymers have potential applications in phase separation membranes, packagings, coatings and blend compatabilizers.



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Experimental

Materials

All reagents were purchased from Aldrich and used as received except when reported. Styrene, benzene, tetrahydrofuran and ethyl 4-chlorobutyrate were distilled prior to use. 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene was purified by flash chromatography until the ^{1}H NMR corresponded to the expected structure and the GCMS showed > 99% purity.

Characterization

General. ^{1}H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ on a VXR-300 at 300 MHz and 75.5 MHz, respectively. A Varian GC fitted with a Finnigan Mat Magnum mass spectrometer was used for product identification. High-resolution mass spectrometry was performed with a Kratos MS50TC at a resolution (*R*) of 14,300 in electron impact (EI) mode with an electron beam energy of 70 eV.

Synthetic Procedures

Synthesis of 2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene.

Ethyl δ-iodobutyrate.[8] Acetone (700 mL) and sodium iodide (90 g, 600 mmol) were added to a one-necked, 1.0 L round-bottom flask, equipped with a water condenser. Ethyl δ-chlorobutyrate (14 mL, 100 mmol) was then added and the mixture was refluxed for 12 hours. The solution was cooled and concentrated using a rotary evaporator. Approximately 100 mL of water was added to dissolve the salt. The aqueous layer was extracted twice with diethyl ether (150 mL), washed with brine, dried over magnesium sulfate and filtered. The extracts were concentrated and distilled over copper powder under reduced pressure to provide the liquid product (23.5 g, 98 %yield). ^{1}H NMR (**N8**), ($CDCl_3$): δ 1.25 (t, 3H; *J* = 6 Hz, -C$\underline{H}_3$), 2.10 (dd, 2H; *J* = 6 and 9 Hz, -C$\underline{H}_2$), 2.45(t, 2H; *J* = 9 Hz, -C$\underline{H}_2$-CO_2), 3.22 (t, 2H; *J* = 6 Hz, -C$\underline{H}_2$I), 4.14 (q, 2H; *J* = 6 Hz, -OC$\underline{H}_2$). ^{13}C NMR (**N9**), ($CDCl_3$): δ 6 (-$\underline{C}H_3$), 14 (-$\underline{C}H_2$), 29 (-$\underline{C}H_2$-CO_2), 35 (-$\underline{C}H_2$-I), 61 (-O$\underline{C}H_2$), 172 (-$\underline{C}O_2$).

2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene.[8,21,22] Zinc granules (30 mesh, 26 g, 400 mmol) and 80 mL of tetrahydrofuran (THF) were added to a flame-dried argon-purged three-necked, 250 mL round-bottom flask. The zinc was activated by refluxing in 8 mL of 1,2-dibromoethane. Ethyl δ-iodobutyrate (24 g, 100 mmol) was added and the reaction was heated to 50 °C for 24 hours. Before the next step, the alkyl zinc iodide solution was cooled to room temperature. Lithium chloride (8.5 g, 200 mmol) was added to a two-necked, 500 mL round-bottom flask. The flask was evacuated and flame dried several times to remove any excess water from the salt and from the surface. After purging with argon, copper cyanide (9.0 g, 100 mmol) was added to the flask under a strong flow of argon. The flask was then evacuated and purged with argon three times. After the addition of 80 mL THF, the solution was cooled to –30 °C and the alkyl zinc iodide solution was added via cannula. The solution was warmed to 0 °C, held at that temperature for 10 minutes and cooled to –78 °C. This was followed by the dropwise addition of 1,4-dichloro-2-butyne (4.4 mL, 45 mmol). The solution was stirred for 12 hours as it warmed to room temperature. The flask was opened and its contents were poured into a saturated ammonium chloride solution to quench any residual cuprate. The aqueous layer was extracted twice with 150 mL of diethyl ether, washed with brine and finally washed with sodium thiosulfate to remove any iodide ions from the solution. The organic layer was dried over magnesium sulfate, filtered and concentrated under vacuum to provide a crude oil. The product was purified by filtration with basic alumina on a sintered glass funnel (the eluent was a 15% ethyl acetate in hexanes mixture) followed by column chromatography (the eluent was a 5% ethyl acetate in hexanes mixture gradually increasing to a 15% ethyl acetate in hexanes mixture). Yield: 82%. Purity > 99% by GCMS (**M3**). ^{1}H NMR (**N10**), ($CDCl_3$): δ 1.26 (t, 6H; J = 6 Hz, -C$\underline{H}_3$), 1.80 (q, 4H; J = 9 Hz, -C$\underline{H}_2$), 2.28 (t, 4H; J = 9 Hz, -C$\underline{H}_2$-CO_2), 2.30 (t, 4H; J = 9 Hz, -C$\underline{H}_2$-C=), 4.12 (q, 4H; J = 6 Hz, -OC$\underline{H}_2$), 4.96 (d, 2H, -C$\underline{H}$=C), 5.11 (d, 2H, -C$\underline{H}$=C). ^{13}C NMR (**N11**), ($CDCl_3$): δ 14 (-$\underline{C}H_3$), 24 (-$\underline{C}H_2$), 33 (-$\underline{C}H_2$-CO_2), 34 (-$\underline{C}H_2$-C=), 60 (-O$\underline{C}H_2$), 113 (-$\underline{C}H_2$=C), 146 (-$\underline{C}$=CH_2), 174 (-$\underline{C}O_2$). High-resolution mass spectrometry (**M4**): theoretical mass 282.183676, measured mass 280.98242, deviation 2 ppm.

Initiator Synthesis.

Synthesis of *N-tert*-butyl-α-*iso*propylnitrone.[19] To a 1 L round-bottom flask, 2-methyl-2-nitropropane (20.6 g, 200 mmol) and *iso*-butyraldehyde (14.4 g, 200 mmol) were added while stirring. To this mixture was added ammonium chloride (11.8 g, 220 mmol) and 400 mL of water. The reaction was cooled to 0 °C in an ice bath and 300 mL of ethyl ether was added to dissolve the ammonium chloride. Zinc powder (52 g, 800 mmol) was added in small portions over an hour. After stirring at room temperature for 24 hours, the mixture was filtered through a sintered glass filter that contained one inch of celite. The cake was washed generously with water and dichloromethane and the product was extracted four times with dichloromethane. The organic layers were combined and washed with a saturated sodium chloride solution. The product was dried over magnesium sulfate, filtered and concentrated using a rotary evaporator (water bath is not to exceed 30 °C) to obtain a clear liquid in 80% yield (2.3 g, 16 mmol). ^{1}H NMR (**N12**), ($CDCl_3$): δ 1.21 (s, 9H; -C(C$\underline{H}_3$)$_3$), 1.42 (d, 6H; -

$C(C\underline{H}_3)_2$), 2.10 (m, 1H, $-C\underline{H}-(CH_3)_2$), 6.52 (d, 1H; $-C\underline{H}-CH(CH_3)_2$). ^{13}C NMR (**N13**), ($CDCl_3$): δ 26.1 ($-C(\underline{C}H_3)_3$), 28.5 ($-C(\underline{C}H_3)_2$), 30.7 ($-\underline{C}-(CH_3)_3$), 69.2 ($-\underline{C}H-(CH_3)_2$), 139.6 ($-\underline{C}H-CH(CH_3)_2$).

Synthesis of 2,2,5-trimethyl-4-phenyl-azahexane-3-nitroxide.[20] To a 500 mL, flame dried, two neck round-bottom flask equipped with a vacuum adapter and an addition funnel, *N-tert*-butyl-α-*iso*propylnitrone (21.21 g , 148 mmol) and 170 mL of tetrahydrofuran (THF) were added while stirring. The reaction was cooled to 0 °C in an ice bath and 120 mL of phenyl magnesium bromide was added dropwise via the addition funnel. Then the reaction mixture was warmed to room temperature and allowed to stir for twelve hours under argon. The excess grignard reagent was decomposed by the addition of concentrated ammonium chloride while being chilled in an ice bath. The organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The organic layers were combined, dried over magnesium sulfate, filtered and concentrated via rotary evaporation (water bath not to exceed 30 °C). The residue was treated with 800 mL of methanol, 60 mL concentrated ammonium hydroxide and 1.8 g copper acetate (9.2 mmol). A stream of air was bubbled through the mixture for one hour until the solution turned dark blue and then the mixture was concentrated. The residue was dissolved in 800 mL of chloroform, 200 mL of saturated sodium bisulfate and 800 mL of water. The organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The organic layers were combined, washed with saturated sodium bicarbonate solution, dried over magnesium sulfate, filtered and concentrated. The crude product was purified via flash column chromatography. The column was loaded with hexanes then run with hexanes until first spot came through and then run with 98:2 hexanes: ethyl acetate to collect the product. The nitroxide was collected as an orange oil that crystallizes at temperatures below 4 °C in 67% yield (22 g, 99 mmol). ^{1}H NMR (**N14**), ($CDCl_3$): δ 1.20 (d, 6H; -C(C$\underline{H}_3$)$_2$), 1.44 (s, 9H; -C(C$\underline{H}_3$)$_3$), 2.28 (m, 1H, -C$\underline{H}$-(CH_3)$_2$), 3.41 (d, 1H; -C$\underline{H}$-CH(CH_3)$_2$) 725-7.60 (m, 5H, Ph). ^{13}C NMR (**N15**), ($CDCl_3$) in the presence of pentafluorophenyl hydrazine: δ 18.5, 20.5, 21.5, 26.9, 30.2, 31.2, 31.5, 59.1, 63.3, 71.3, 73.4, 126.6, 127.3, 127.8, 128.4, 128.77, 129.5, 136, 141.2, 142.06, 154.3.

Synthesis of 2,2,5-trimethyl-3-(1'-phenylethoxy)-4-phenyl-3-azahexane (I).[20] In a 1000 mL round -bottom flask, air was bubbled through 340 mL of a 1:1 ethanol : toluene solution for one hour. Styrene (3.74 g, 36 mmol) and 2,2,5-trimethyl-4-phenyl-azahexane-3-nitroxide (6.78 g, 30 mmol) were added sequentially to the solution. Jacobsen's catalyst (2.96 g, 4.66 mmol), [*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyaclohexanediamino] manganese (III) chloride, was added in one portion followed immediately by sodium borohydride (2.32 g, 60.8 mmol). The mixture was bubbled through with air for at least six hours. The reaction was then filtered through a sintered glass filter funnel with a bed of silica gel in it. The silica gel was washed with 350 mL of dichloromethane and the solution was evaporated to dryness. Following the evaporation, 100 mL of chloroform was added to the residue and evaporated to remove the remaining ethanol. The crude product was purified by flash column chromatography by initially running with hexanes and then switching to 9:1 hexanes : methylene chloride. The pure product was obtained as a colorless oil in 81% yield (7.9 g, 24.3 mmol). ^{1}H NMR ($CDCl_3$, both diastereomers) (**N16**): δ 0.22 (d, 3H, minor diastereomer), 0.54 (d, 3H, major diastereomer), 0.77 (s, 9H major diastereomer), 0.92 (d, 3H, minor diastereomer), 1.04 (s, 9H, major diastereomer), 1.31 (d, 3H, major diastereomer), 1.54 (d 3H, minor diastereomer), 1.62 (d, 3H, major diastereomer), 2.35 (two m, 2H both diastereomers) 3.29 (d, 1H, minor diastereomer), 3.41 (d, 1H, major diastereomer), 4.90 (q + q, 2H, both diastereomers), 7.5-7.1 (m, 20H, aromatic). ^{13}C NMR ($CDCl_3$, both diastereomers) (**N17**): δ 21.1, 21.3, 22.1, 23.2, 23.3, 24.8, 28.3, 28.5, 31.7, 32.1, 60.5, 60.6, 72.2, 72.3, 82.9, 83.6, 126.3, 126.4, 126.7, 127.1, 127.3, 127.4, 127.5, 128.2, 131.0, 142.4, 142.6, 145.1, 145.9.

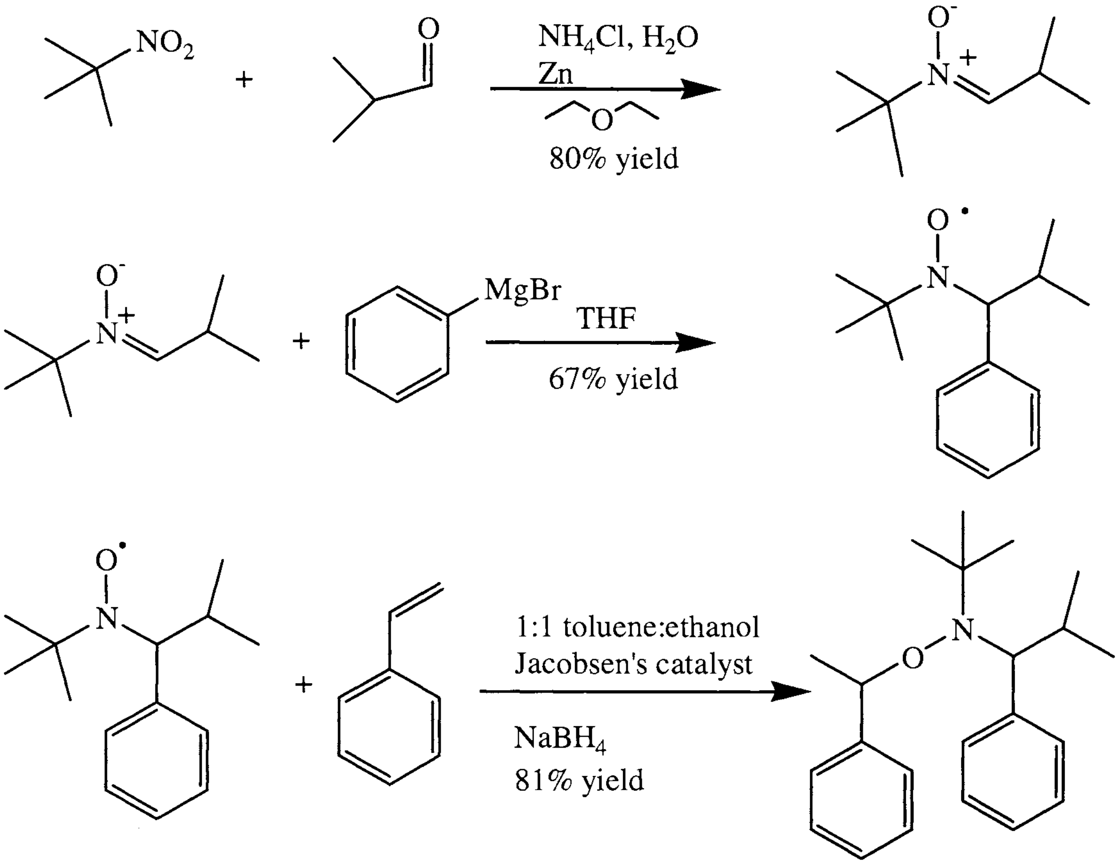
Homopolymer Synthesis.

General procedure for bulk and solution polymerization of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene. EOBD (1.0 g, 3.54 mmol), 1.0 mole % **I** (11.5 mg, 0.0354 mmol), solvent (for solution polymerizations only), free nitroxide (mole % based on initiator concentration) and a stir bar were added to an ampoule. After three freeze-pump-thaw cycles, the ampoule was sealed under argon and then placed in a constant temperature oil bath for the allotted time. The polymer was precipitated twice from dichloromethane into hexanes. The polymer was dried under vacuum and then analyzed. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 6H; CH_3), 1.68 (m, 4H; $-C\underline{H}_2$), 2.05 (t, 4H, $-C\underline{H}_2-CO_2$), 2.09 (t, 4H, $-C\underline{H}_2-C=$), 2.29 (t, 4H, $-C\underline{H}_2-C=$), 4.12 (q, 4H; $-OC\underline{H}_2$). ^{13}C NMR ($CDCl_3$): δ 14 ($-\underline{C}H_3$), 31 ($-\underline{C}H_2-CO_2$), 31.5 ($-\underline{C}H_2C=$), 34 ($-\underline{C}H_2-C=$), 60 ($-O\underline{C}H_2$), 133 ($-\underline{C}=C$), 174 ($-\underline{C}O_2$). Elemental analysis: 67.25% C, 8.86% H.

RESULTS AND DISCUSSIONS

2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene (EOBD) was synthesized according to Beery *et al.*[8] The synthesis of the alkoxyamine initiator, **I**, was performed according to Benoit *et al.*[20] and is shown in Scheme 1. The first step reductively condensed 2-methyl-2-nitropropane to *N-tert*-butyl-α-*iso*-propyl nitrone. The nitrone then underwent a Grignard reaction with phenyl magnesium bromide to form the free nitroxide (2,2,5-4-phenyl-3-azahexane-3-nitroxide), which was converted to **I** in the presence of Jacobsen's catalyst, styrene and sodium borohydride. Purification of the final product yielded a clear liquid in 38% overall yield. This initiator was important because of its ability to polymerize not only diene-based monomers, but functionalized monomers as well. It is through this combination that we chose to utilize this initiator for our functionalized butadiene monomers.

Previously, we have seen the formation of the Diels-Alder product during free radical polymerization of our monosubstituted butadienes with as much as 10% Diels-Alder product formed at 125 °C.[16] In deciding which functionalized 1,3-butadiene to first explore the nitroxide mediated polymerization, we attempted to polymerize 2-(*N,N*-dipropylaminomethyl)-1,3-butadiene. Upon polymerization using 1.0 mole % **I** at 125 °C, there was 33% conversion to polymer and 25% conversion to the Diels-Alder product as verified by ^{1}H NMR (Table 1). Lowering the temperature did decrease the amount of Diels-Alder product formed (6% and a negligible amount when reducing to 100 °C and 75 °C, respectively) but it also greatly decreased the conversion to the polymer (12 to 1.7%). EOBD was chosen because we have not seen any formation of the Diels-Alder product with our disubstituted monomers. We attribute the lack of the Diels-Alder product to the steric bulk of the monomer. In addition to the lack of the Diels-Alder product, poly(EOBD) is easy



Scheme 1. Synthesis of 2,2,5-trimethyl-3-(1'-phenylethoxy)-4-phenyl-3-azahexane, the alkoxyamine initiator.

to process and characterize. Poly(EOBD) is stable in light and lacks the solvent resistance that we have seen with poly[2,3-bis(cyanopropyl)-1,3-butadiene].

Previously our group has explored the bulk and solution polymerization of EOBD using different initiators and temperatures.[8] At 125 °C, high molecular weights were achieved (8.0×10^4 –13.2×10^4 g/mol). However the PDIs were large as well, ranging from

Table 1. Homopolymerization of 2-(*N,N*-dipropylaminomethyl)-1,3-butadiene using 1.0 mole % initiator for 48 hours.

Entry	Temp. °C	Conv. wt. %[a]	% Diels Alder formed [b]
16	125	33	25
17	100	12	6
18	75	1.7	negligible

[a] calculated by (weight of polymer/weight of monomer) x 100
[b] determined by ^{1}H NMR

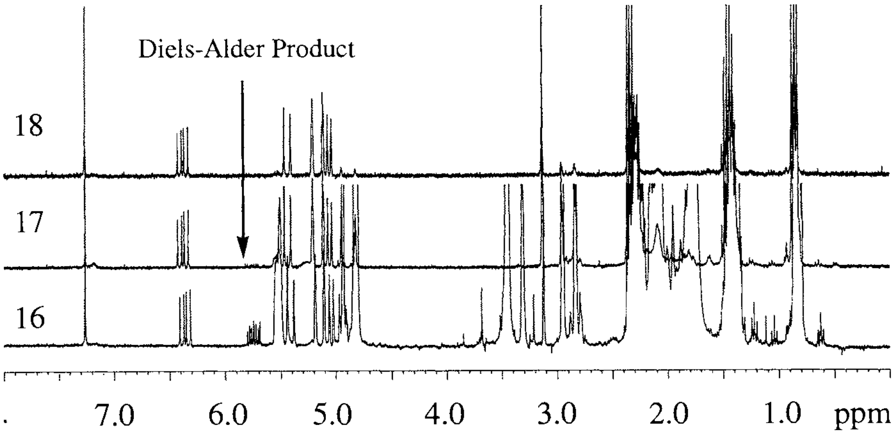
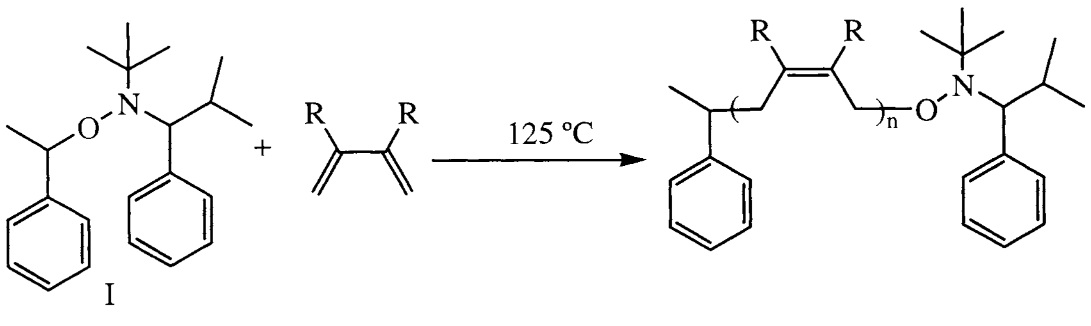


Figure 1. ^{1}H NMR spectra of 2-(*N,N*-dipropylaminomethyl)-1,3-butadiene (16-18).

2.57 to 3.94 depending on the initiator concentration. Through the use of the alkoxyamine initiator (Scheme 2), we have been able to decrease the PDIs of this homopolymer to as low as 1.10. Table 2 shows the molecular weight data for the nitroxide mediated polymerization of EOBD at various times with calculated molecular weights. The calculated molecular weights were determined by multiplication of the conversion and the target molecular weight. The conversions of polymers 19 through 21 increased from 18 to 52% with increasing time (12 to 48 h) as expected for a controlled free radical polymerization. The target molecular weight was 2.8×10^4 g/mol for all samples based on quantitative conversions. In all cases, the molecular weight was greater than the calculated molecular weight. We believe this may be due to termination by coupling. The PDIs for these samples were also very low (1.1-1.26) in comparison with traditional free radical polymerization of this monomer. After 36 h, the polymerization appeared to shut down as evidenced by the lack of increase in molecular weight and conversion after this time. The thermal data for these materials followed normal trends. As the molecular weight increases from 1.15×10^4 to 2.85×10^4 g/mol, the 5% weight loss in air increased from 283 °C to 308 °C and the glass transition temperature of this material remained at –37 °C.[8]

In an effort to overcome the problem of polymerization termination, free nitroxide was added to shift the equilibrium towards the nitroxide end-capped polymer. The mechanism for this polymerization is shown in Scheme 3. By increasing the free nitroxide concentration, the rate of polymerization should decrease, but should still be greater than the rate of termination. The rate of polymerization (Equation 1) is first order while the rate of



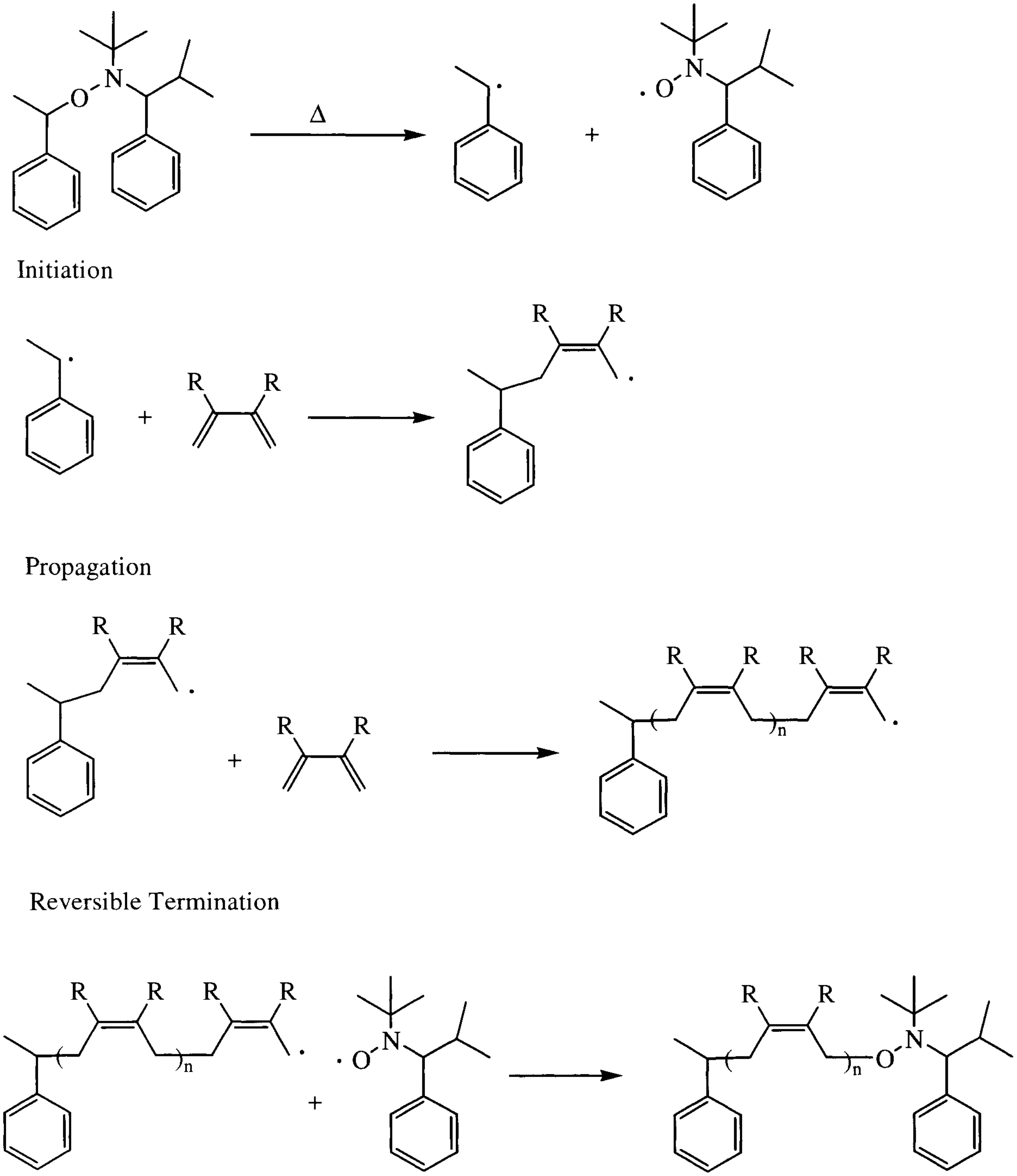
Scheme 2. Nitroxide mediated polymerization of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene.

Table 2. Nitroxide mediated polymerization of EOBD using 1.0 mole % initiator with a target of 2.8 x 10^4 g/mol.

Entry #	Time h	$<M_n>^a$ x 10^{-3} g/mol	PDI[a]	Calc.[b] M_n x 10^{-3} g/mol	Conv. wt. %	GPC G#
19	12	14.9	1.10	5.1	18	**G15**
20	24	11.5	1.19	7.6	27	**G16**
21	36	32.7	1.21	13.4	48	**G17**
22	48	22.9	1.35	14.7	52	**G18**
23	60	28.2	1.53	16.6	59	**G19**
24	72	28.5	1.65	16.1	57	**G20**

[a] run in THF, by GPC based upon polystyrene standards
[b] calculated based on conversion multiplied by target molecular weight

termination is second order (Equation 2), thus even though the rate of termination increases, the ratio of the rate of polymerization to the rate of termination (Equation 3) will increase.[23] The resulting system obtained higher conversions with more reasonable molecular weights, when compared to the calculated molecular weights, as seen in Table 3. For 1.0 mole % free nitroxide added, the polymer reached 71% conversion at 48 hours, whereas in the absence of free nitroxide 59 % yield was the greatest reached. The molecular weights at 1.0 mole % initiator also show greater correlation to those calculated based upon conversion. However, at lower initiator concentrations of 0.5 mole % and 0.1 mole %, the polymerizations resulted in termination at 24 hours with 49 and 20% yield, respectively. For 0.5 mole % there is also better correlation between the experimental molecular weights and the calculated molecular weights than was seen previously with 1.0 mole % in the absence of free nitroxide but this



Scheme 3. Proposed mechanism for the nitroxide mediated polymerization.

trend was not seen with the 0.1 mole % initiator concentration. The 0.1 mole % initiator concentration showed lower experimental molecular weights than calculated, which was an indication that the polymerization has some degree of control. However, it lacked the desired control. In all cases, the PDIs are lower, ranging from 1.16 to 1.54, than was seen in traditional free radical polymerization of this monomer but it was not as low as many of the polymers formed in the absence of free nitroxide. One possible explanation for this observed trend is that too much free nitroxide could have been added and thus shifted the equilibrium too far causing the polymer not to propagate.

$$R_p = k_p [M^{\cdot}][M] \qquad \text{Equation 1}$$

$$R_T = 2k_T[M^{\cdot}]^2 \qquad \text{Equation 2}$$

$$R_p/R_T = k_p[M]/2k_T[M^{\cdot}] \qquad \text{Equation 3}$$

One way to test whether too much free nitroxide was added was to decrease the free nitroxide concentration from 5 mole % of the initiator to 2.5 mole %. In this system there was evidence that the amount of free nitroxide needed was dependent on the initiator concentration. In the 5 mole % free nitroxide experiments the best results were seen with 1.0 mole % initiator concentration. In the 2.5 mole % free nitroxide (Table 4), 1.0 mole % initiator molecular weight data was more similar to the data seen from the absence of free nitroxide, in that the conversion plateaus at 59%. The conversions for the lower initiator concentrations of 0.5 mole % and 0.1 mole % were as high as 59% and 70%, respectively. However, with those higher conversions came greater PDIs, as high as 1.64, and far less correlation between experimental molecular weight and calculated molecular weight.

Table 3. Nitroxide mediated polymerization of EOBD using 5.0 mole % free nitroxide.

Entry #	% I[a]	Time h	$\langle M_n \rangle$[b] x 10^{-3} g/mol	PDI[b]	Calc.[c] M_n x 10^{-3} g/mol	Conv. wt. %	GPC G#
25	1.0	24	17.5	1.16	12.6	45	**G21**
26	1.0	48	22.6	1.32	20.0	71	**G22**
27	0.5	24	24.7	1.37	27.6	49	**G23**
28	0.5	48	16.6	1.53	26.5	47	**G24**
29	0.1	24	25.2	1.54	50.8	18	**G25**
30	0.1	48	39.5	1.33	57.5	20	**G26**

[a] % I = mole percent initiator
[b] run in THF, by GPC based upon polystyrene standards
[c] calculated based on conversion multiplied by target molecular weight

Table 4. Nitroxide mediated polymerization of EOBD using 2.5 mole % free nitroxide.

Entry #	% I[a]	Time h	$\langle M_n \rangle$[b] x 10^{-3} g/mol	PDI[b]	Calc.[c] M_n x 10^{-3} g/mol	Conv. wt. %	GPC G#
31	1.0	24	22.6	1.17	16.1	57	**G27**
32	1.0	48	17.9	1.37	16.6	59	**G28**
33	0.5	24	29.6	1.31	25.8	46	**G29**
34	0.5	48	21.6	1.58	33.2	59	**G30**
35	0.1	24	28.4[d]	?	66.6	24	**G31**
36	0.1	48	14.8	1.64	211.5	70	**G32**

[a] % I = mole percent initiator
[b] run in THF, by GPC based upon polystyrene standards
[c] calculated based on conversion multiplied by target molecular weight
[d] molecular weight is $\langle M_p \rangle$

One explanation for this lack of control could be that in bulk polymerization as viscosity increases, hot spots can form. In order to explore this theory, solution polymerizations were performed, shown in Table 5. For 1.0 mole % initiator concentration in 1:1 volume ratio monomer: solvent, as time increased the molecular weight did not change significantly from 24 to 48 hours, maintaining a molecular weight around 1.6 x 10^4 g/mol, but did increase to 2.9 x 10^4 g/mol at 72 hours. The conversion from 24 to 72 hours also did not increase. The PDIs did increase from 1.1 to 1.34, which were not as high as the PDI of 1.65 in bulk polymerization at 72 hours under the same conditions. When the monomer to solvent ratio was increased to 2:1, the conversion increased to 53 %, the molecular weight increased to 2.2 x 10^4 g/mol and the PDI increased slightly to 1.24. However, in all solution polymerizations the desired correlation between the calculated molecular weights and the experimental molecular weights was not seen.

In examining how solvent affects the polymerization at lower initiator concentrations, there was not a significant difference in molecular weights or conversions between the bulk polymerization and solution polymerization of EOBD using 0.1 mole % initiator. With the addition of 1:1 THF, the PDI did decrease significantly from 1.55 to 1.24. However, if the solvent ratio was decreased to 2:1 monomer to solvent the PDI jumped to 2.37, but the conversion increased to 38% at 48 h. With the addition of 5 mole % free nitroxide, there was not a significant difference between this polymer's data and that of the bulk homopolymer. In all cases of 0.1 mole % initiator, the experimental molecular weights were lower than the calculated molecular weights.

The solution polymerization did produce some higher molecular weight materials but still did not result in controlled polymerizations. One reason for this may be due to the lack

Table 5. Nitroxide mediated solution polymerization of EOBD.

Entry #	% I[a]	Time h	Solvent[b]	$\langle M_n \rangle$[c] x 10^{-3} g/mol	PDI[c]	Calc.[c] M_n x 10^{-3} g/mol	Conv. wt. %	GPC G#
37	1.0	24	1:1 THF	16.3	1.11	8.5	30	**G33**
38	1.0	48	1:1 THF	15.5	1.20	9.0	32	**G34**
39	1.0	72	1:1 THF	28.9	1.34	9.9	35	**G35**
40	1.0	48	2:1 THF	21.9	1.24	14.9	53	**G36**
41	0.1	48	None	26.5	1.55	35.8	13	**G37**
42	0.1	48	1:1 THF	23.8	1.25	31.0	11	**G38**
43	0.1	48	2:1 THF	56.1	2.37	107.2	38	**G39**
44	0.1[d]	48	1:1 THF	28.6	1.52	42.3	15	**G40**

[a] % I = mole percent initiator
[b] monomer: solvent ratio by volume
[c] run in THF, by GPC based upon polystyrene standards
[d] calculated based on conversion multiplied by target molecular weight
[e] 5 mole % free nitroxide added

of control of the endcapping process. Acetic anhydride should interact with the nitrogen-oxygen bond to facilitate the easier removal of the endcap, as well as the breaking apart of the initiator. It is through this interaction that the free radical polymerization should occur at a faster rate and thus give the process a higher degree of control. Table 6 shows the results of adding 2 mole % acetic anhydride to the polymerization reaction. Higher conversions of 74 and 86% were obtained using 1.0 mole % initiator at 24 and 48 hours as well as greater conversions for 0.5 and 0.1 mole %, as high as 76 and 55%, respectively. The PDIs are lower than traditional free radical techniques at this temperature ranging from 1.31 to 1.97, increasing as the initiator concentration decreased and the time increased.

Table 6. Nitroxide mediated polymerization of EOBD in the presence of acetic anhydride.[a]

Entry #	% I[b]	Time h	$\langle M_n \rangle$[c] x 10^{-3} g/mol	PDI[c]	Calc.[c] M_n x 10^{-3} g/mol	Conv. wt. %	GPC G#
45	1.0	24	29.5	1.31	20.8	74	**G41**
46	1.0	48	21.9	1.63	24.3	86	**G42**
47	0.5	24	43.8	1.68	28.2	50	**G43**
48	0.5	48	36.8	1.77	42.9	76	**G44**
49	0.1	24	48.4	1.65	62.0	22	**G45**
50	0.1	48	39.9	1.97	155	55	**G46**

[a] acetic anhydride is used at twice the mole % of initiator
[a] % I = mole percent initiator
[c] run in THF, by GPC based upon polystyrene standards
[d] calculated based on conversion multiplied by target molecular weight

CONCLUSIONS

2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene was successfully homopolymerized using the alkoxyamine initiator. Under bulk conditions the polydispersities ranged from 1.10 to 1.65, which is much lower than polydispersities achieved under traditional free radical techniques at 125 °C (2.37-3.94). Prior to this system it was impossible to have controlled polymerizations or block copolymers with functionalized monomers such as EOBD. These preliminary results indicate that EOBD has significant potential in blend compatabilizers, amphiphilic materials, block elastomers and phase separation membranes.

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GENERAL CONCLUSIONS

This thesis is a fundamental study of the free radical polymerization and nitroxide mediated free radical polymerization of functionalized disubstituted 1,3-butadienes. It has been shown that the disubstituted 1,3-butadienes can be synthesized utilizing Rieke chemistry and nucleophilic substitution reactions to produce the monomers in high purity and high yield.

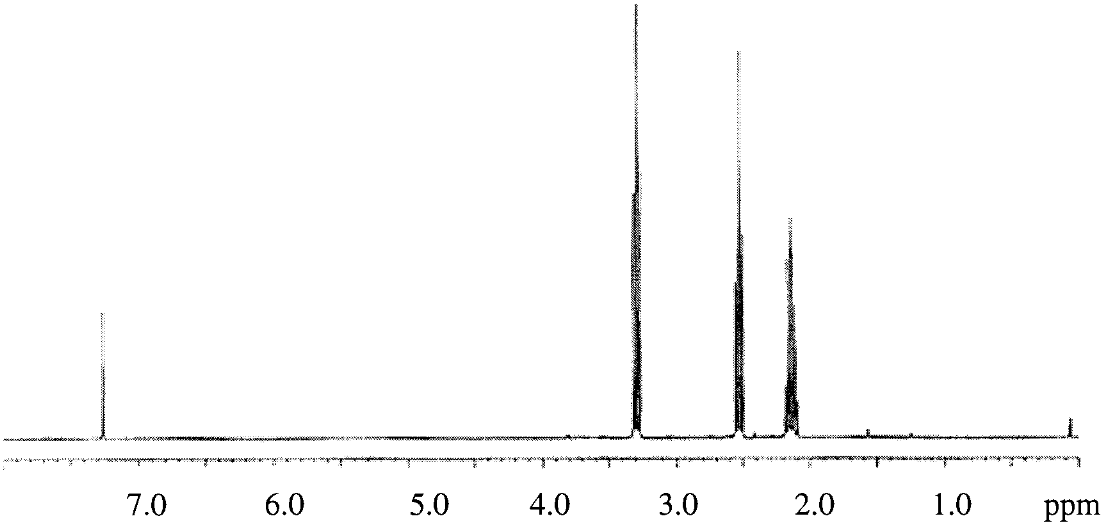
Poly[2,3-bis(cyanopropyl)-1,3-butadiene], poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] and poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] have been successfully polymerized via free radical bulk and solution polymerization, and the copolymerization behavior was investigated. The reactivity ratios of CPBD with styrene and EOBD were determined by the Mayo-Lewis equation. The cyano-substituted monomer had a higher reactivity than styrene and EOBD. The resulting copolymers' glass transition temperatures were dependent on the copolymer composition and fit the Gordon-Taylor equation. All the copolymers obtained were random, noncrystalline polymers, which showed only one T_g on DSC.

Although this paper focuses on the copolymerization of CPBD with one other monomer, the potential to utilize CPBD as a third monomer in commercial materials, such as SBR and NBR is evident. The high reactivity of CPBD should allow it to add readily to such materials. In addition to the high reactivity, the cyano group's good solvent resistance and thermal stability should lend new properties to the resulting materials while maintaining the flexibility of the rubber. These properties combined into the elastomers should extend the potential applications of these materials to include adhesives, packagings and coatings. the potential applications of this material to include adhesives, packagings and coatings.

2,3-Bis(4-ethoxy-4-oxobutyl)-1,3-butadiene was successfully homopolymerized using the alkoxyamine initiator. Under bulk conditions the polydispersities ranged from 1.10 to 1.65, which is much lower than polydispersities achieved under traditional free radical techniques at 125 °C (2.37-3.94). Prior to this system it was impossible to have controlled polymerizations or block copolymers with functionalized monomers such as EOBD. These preliminary results indicate that EOBD has significant potential in blend compatabilizers, amphiphilic materials, block elastomers and phase separation membranes.

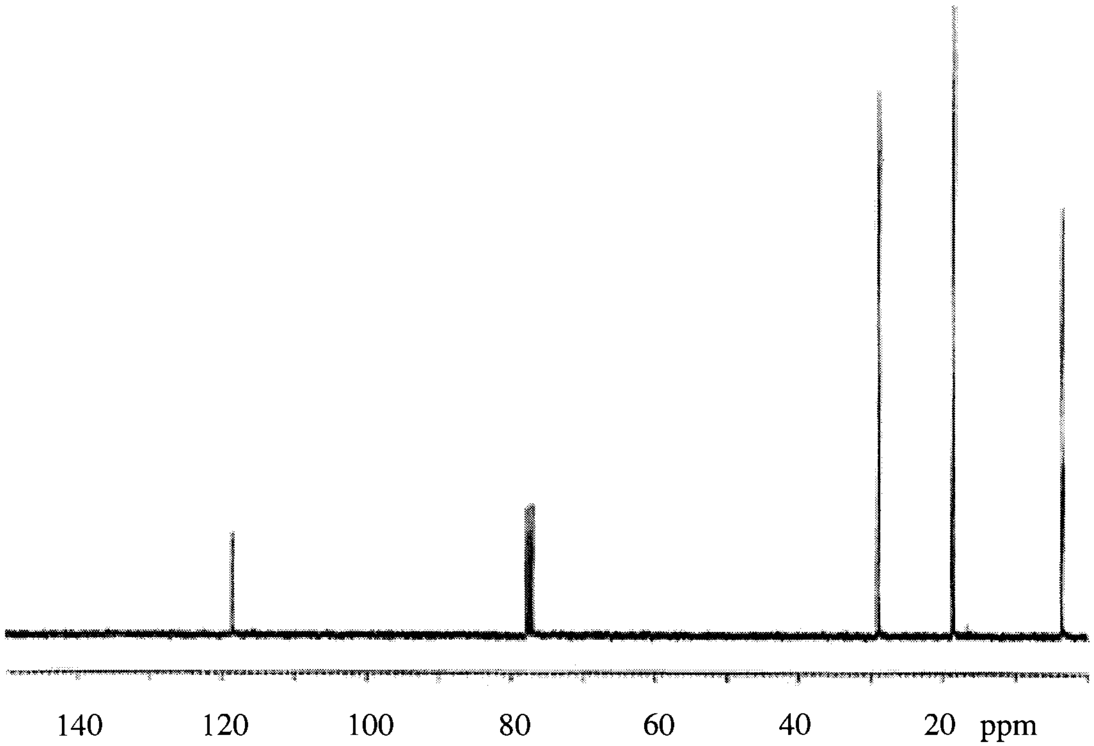
APPENDIX A:

Chapter 1. Data



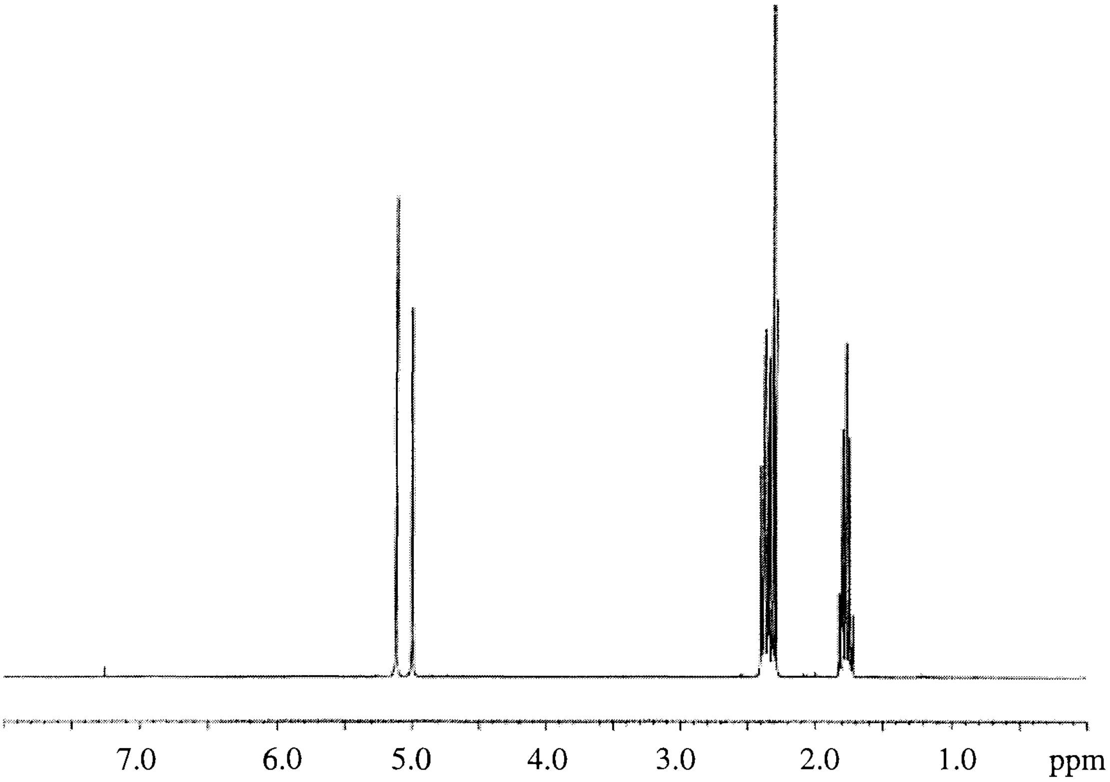
N1

4-Iodobutyronitrile ($CDCl_3$)



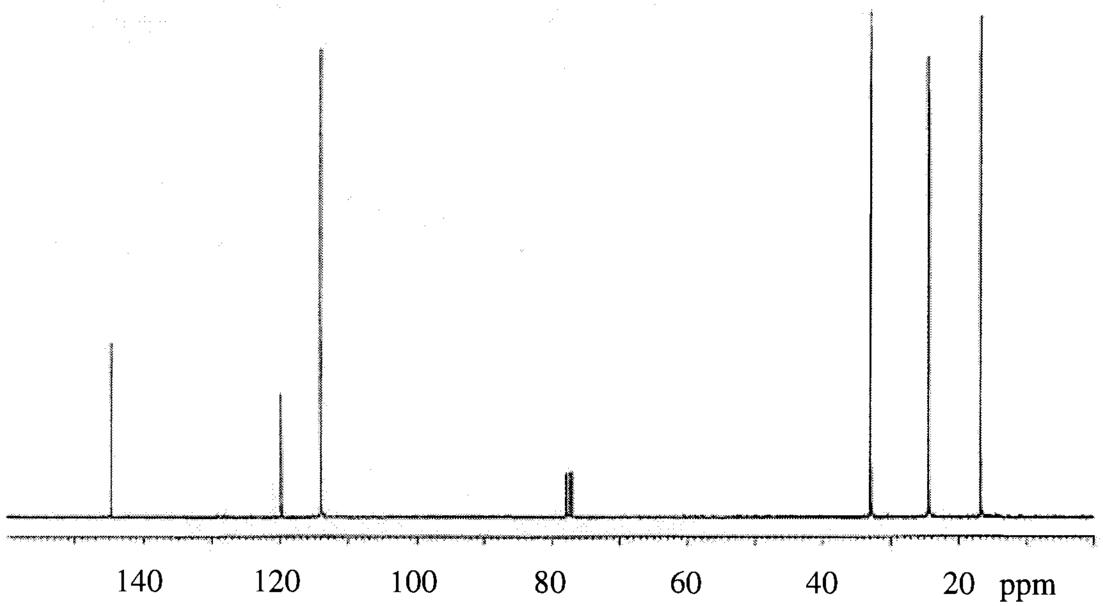
N2

4-Iodobutyronitrile (^{13}C, $CDCl_3$)



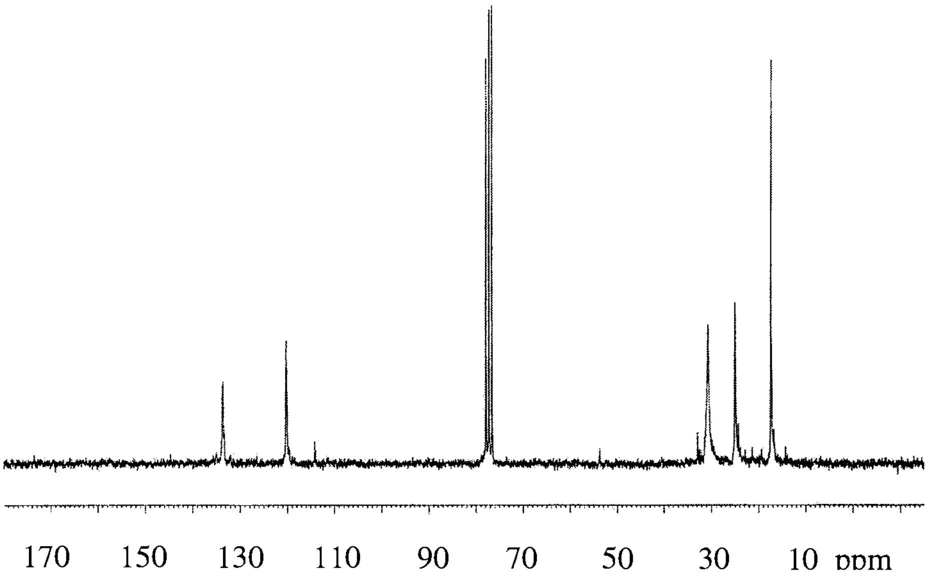
N3

2,3-Bis(cyanopropyl)-1,3-butadiene ($CDCl_3$)



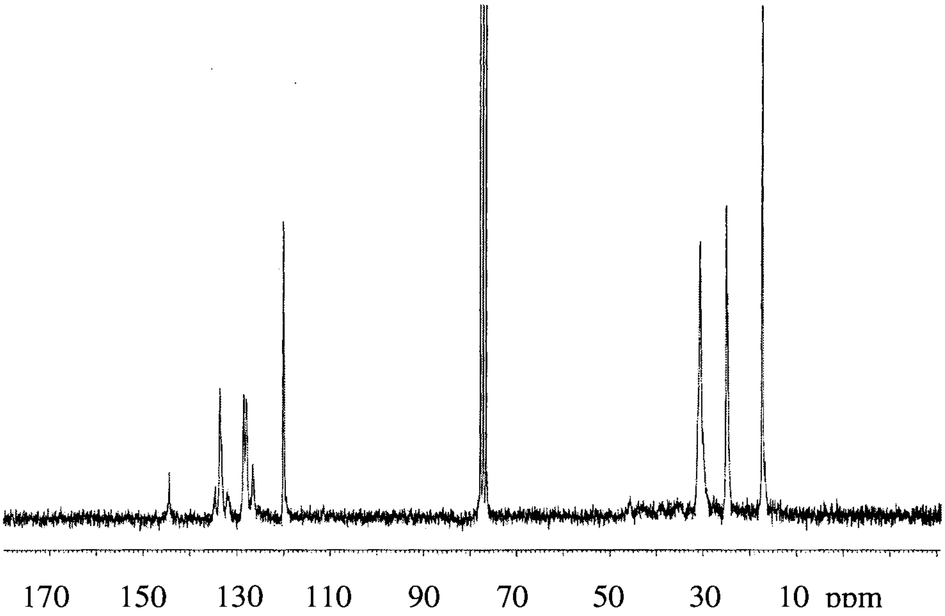
N4

2,3-Bis(cyanopropyl)-1,3-butadiene (^{13}C, $CDCl_3$)



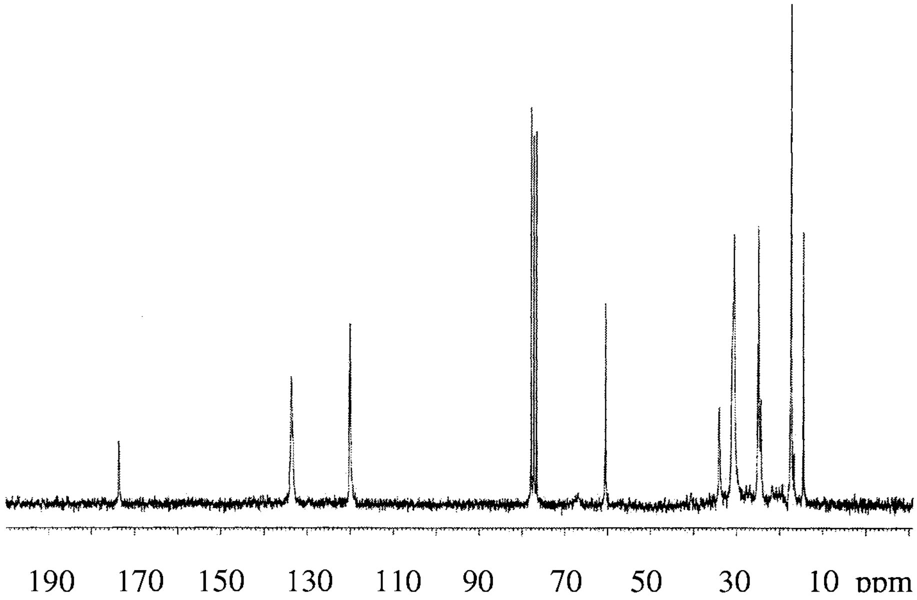
N5

Poly[2,3-bis(cyanopropyl)-1,3-butadiene] (^{13}C, $CDCl_3$)



N6

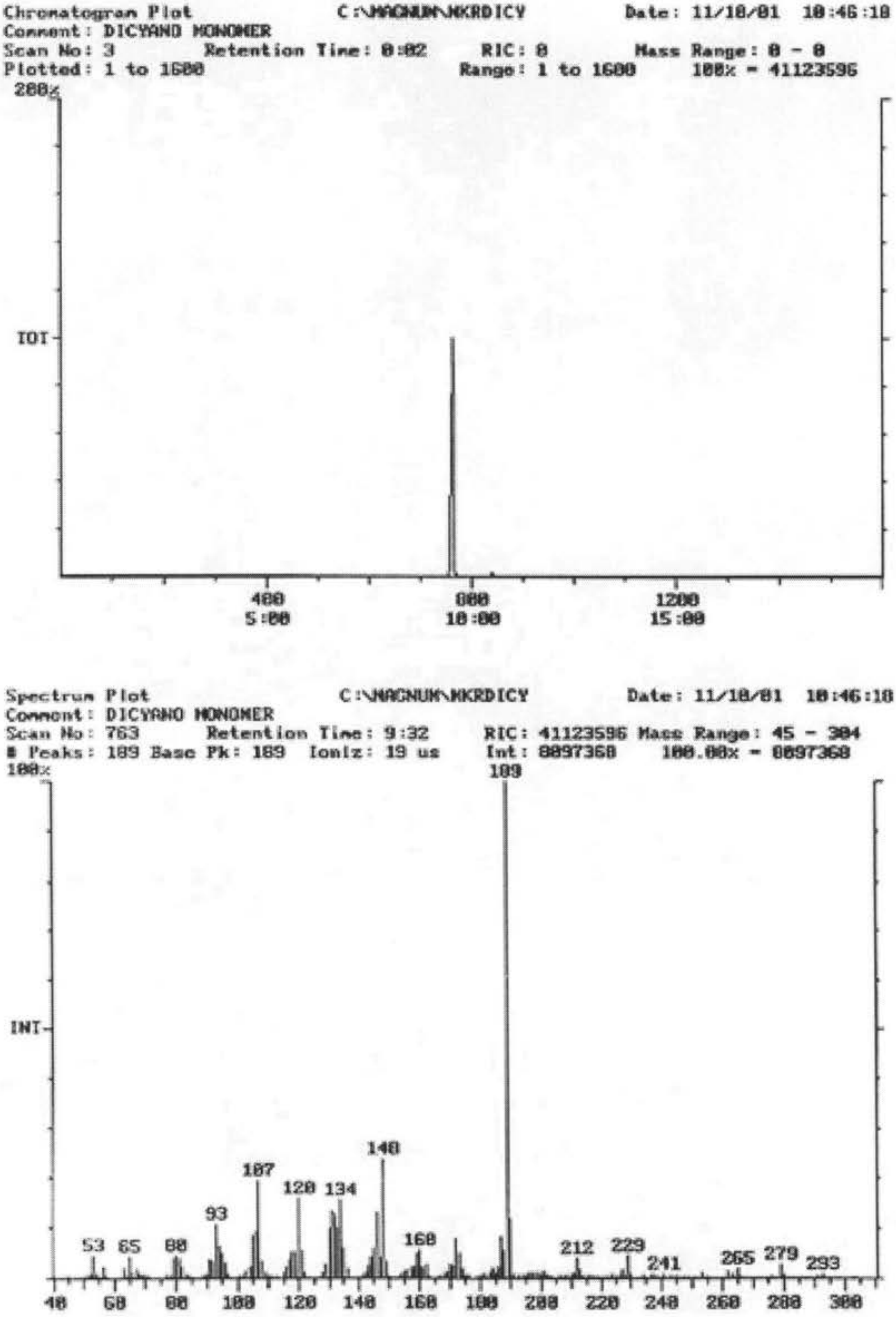
Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] (^{13}C, $CDCl_3$)



N7

Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene]

(^{13}C, CDCl$_3$)



M1

GCMS chromatograph for 2,3-bis(cyanopropyl)-1,3-butadiene

Manual Peak Matching Report
For Accurate Mass Determination

$M^{+\cdot}$

Theoretical mass	Experimental mass	PFK matching mass	Deviation*
188.13135	188.131613	180.98882	1.4 ppm

* The deviation is obtained from the following equation:

$$\text{deviation} = \frac{\text{experimental mass - theoretical mass}}{\text{nominal mass}}$$

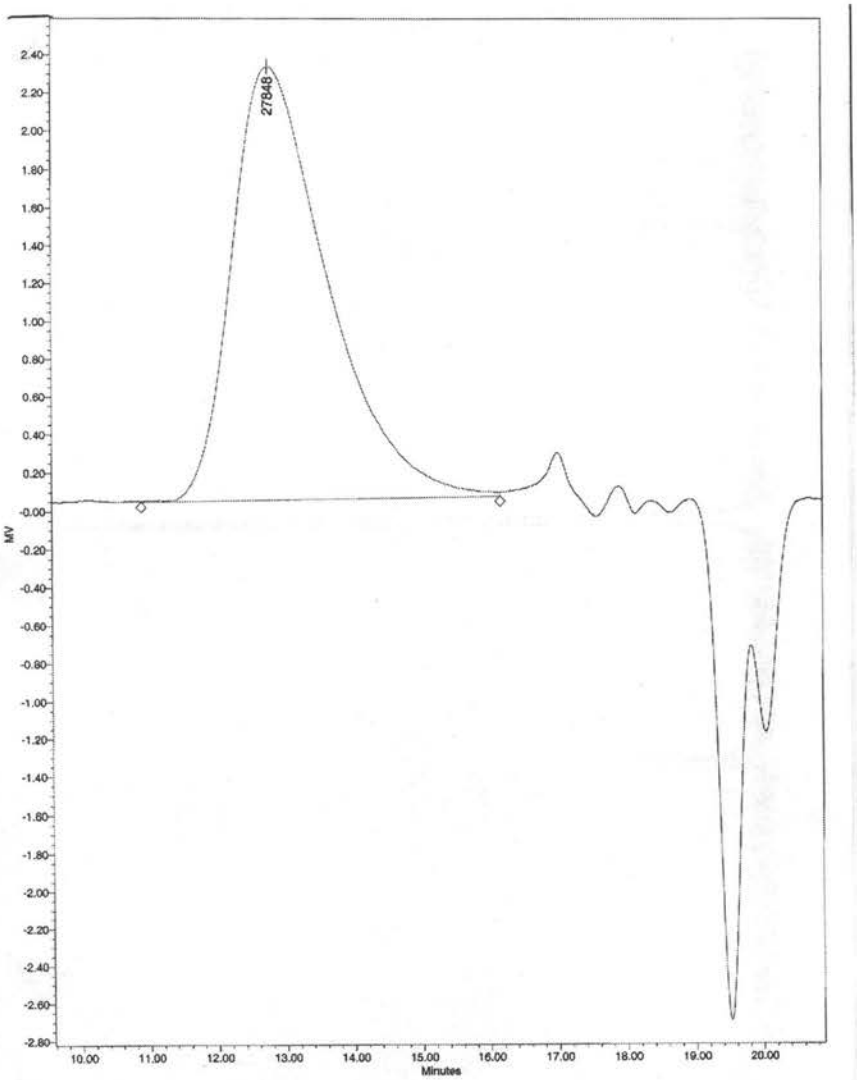
Where nominal mass takes in account only ^{12}C, ^{1}H, ^{16}O, ^{14}N etc...

Theoretical mass correspond to the mass of the most abundant isotope peak

M2

High resolution mass spectrometry for 2,3-bis(cyanopropyl)-1,3-butadiene

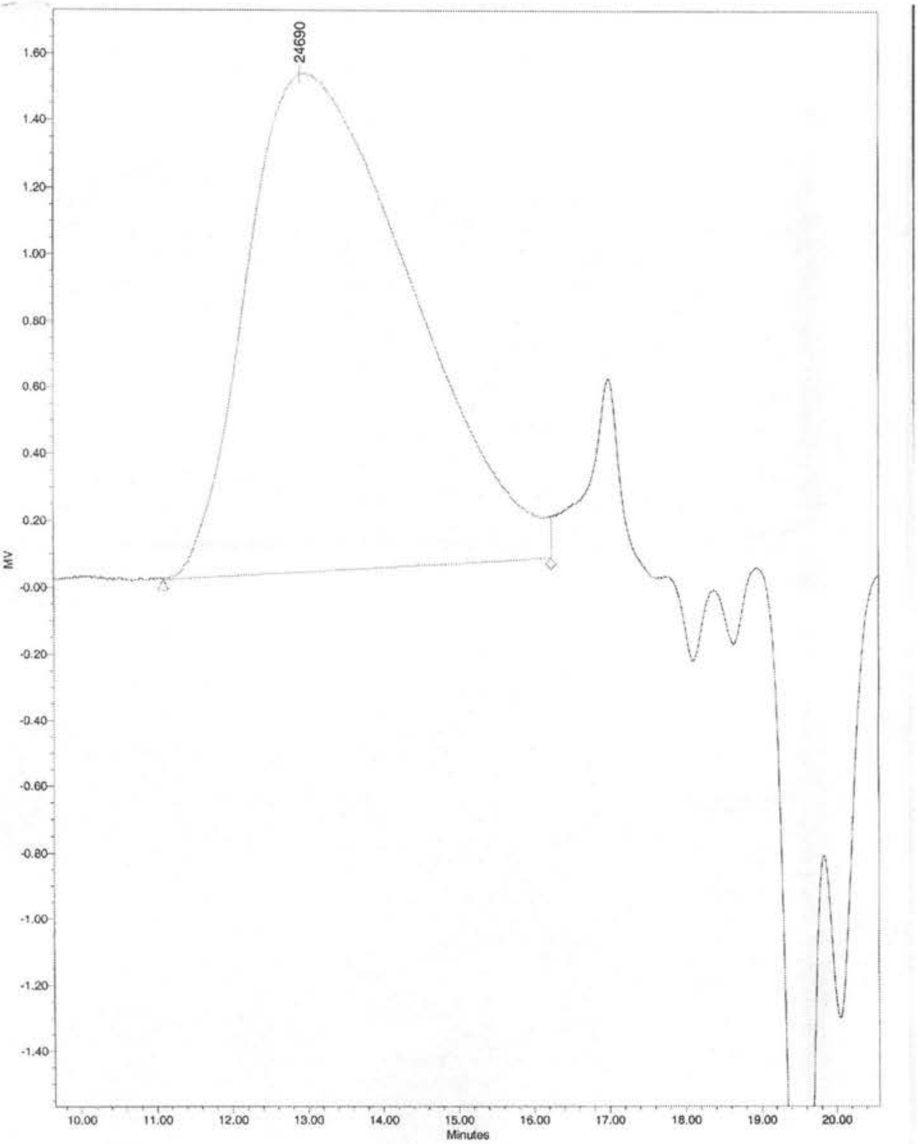
	Distribution Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		12.763	12.763	12.763	15483	24638	27848		31984	38980	1.591317	1.298162	1.582099



G1

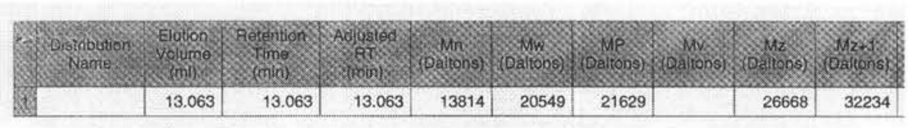
GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene] ($CDCl_3$) from 0.5 mole % AIBN for 1 hour at 75 °C

	Distribution Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		12.907	12.907	12.907	8558	20210	24690		31958	41965	2.361481	1.581281	2.076451

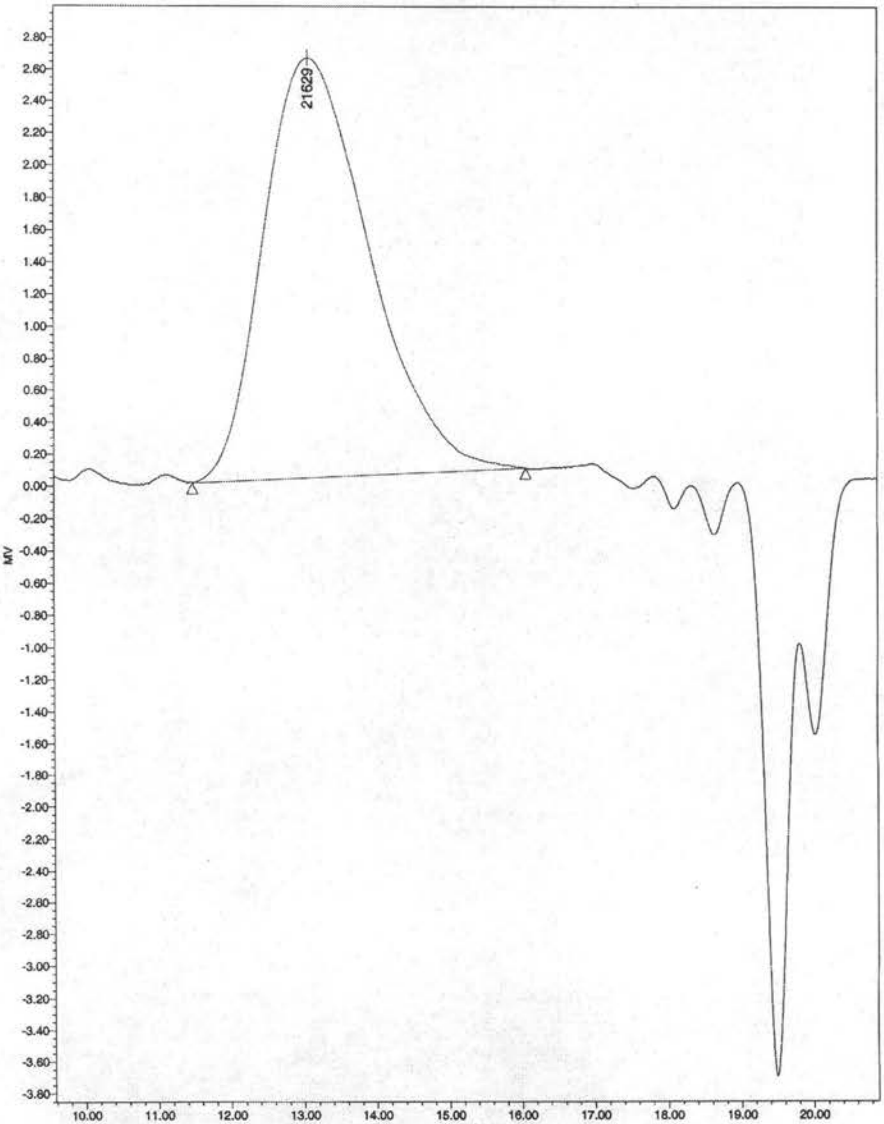


G2

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene] ($CDCl_3$) from 0.5 mole % AIBN for 2 hours at 75 °C

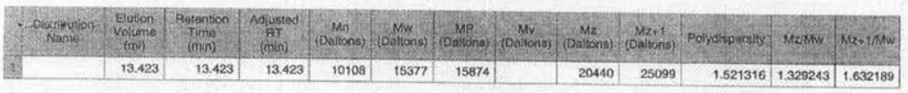


	Distribution Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)
1		13.063	13.063	13.063	13814	20549	21629		26668	32234

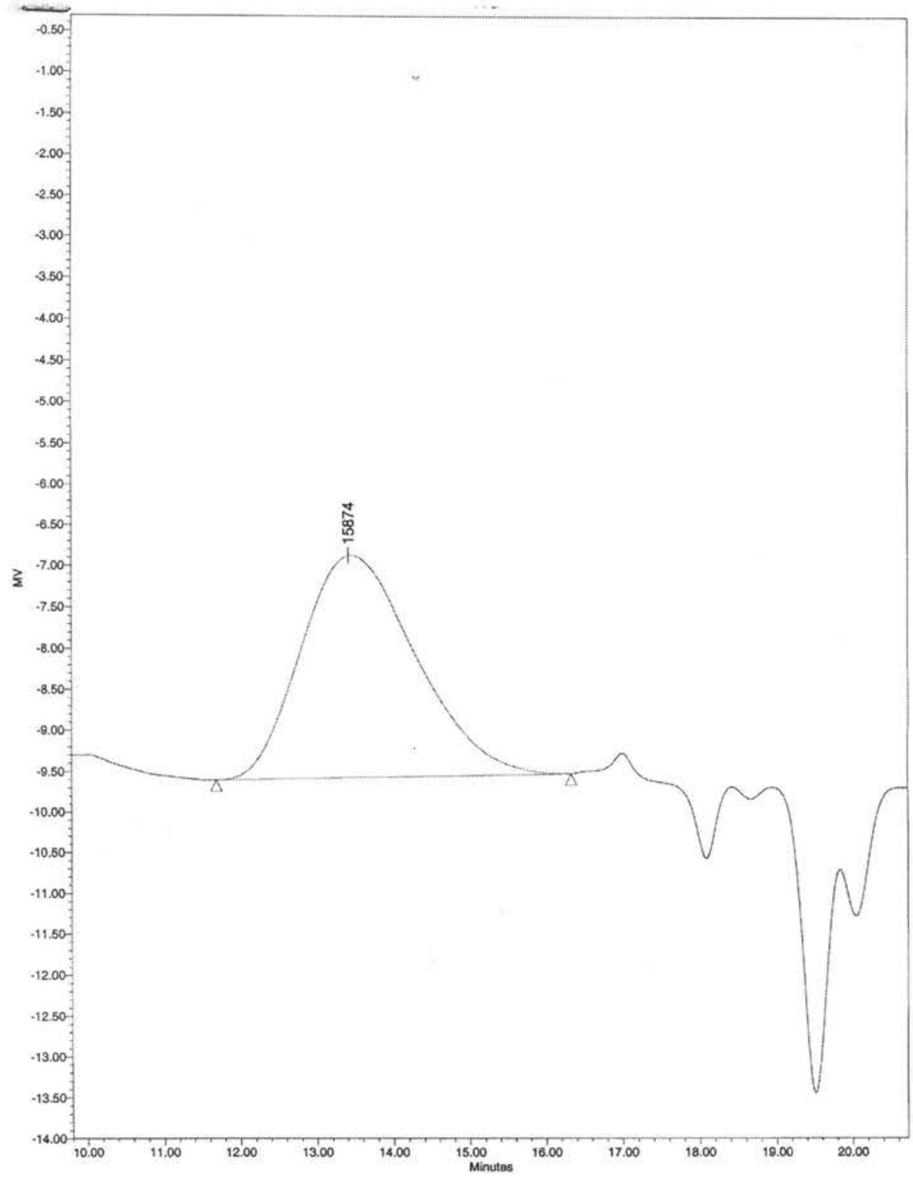


G3

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene] ($CDCl_3$) from 0.5 mole % AIBN for 24 hours at 75 °C in Benzene

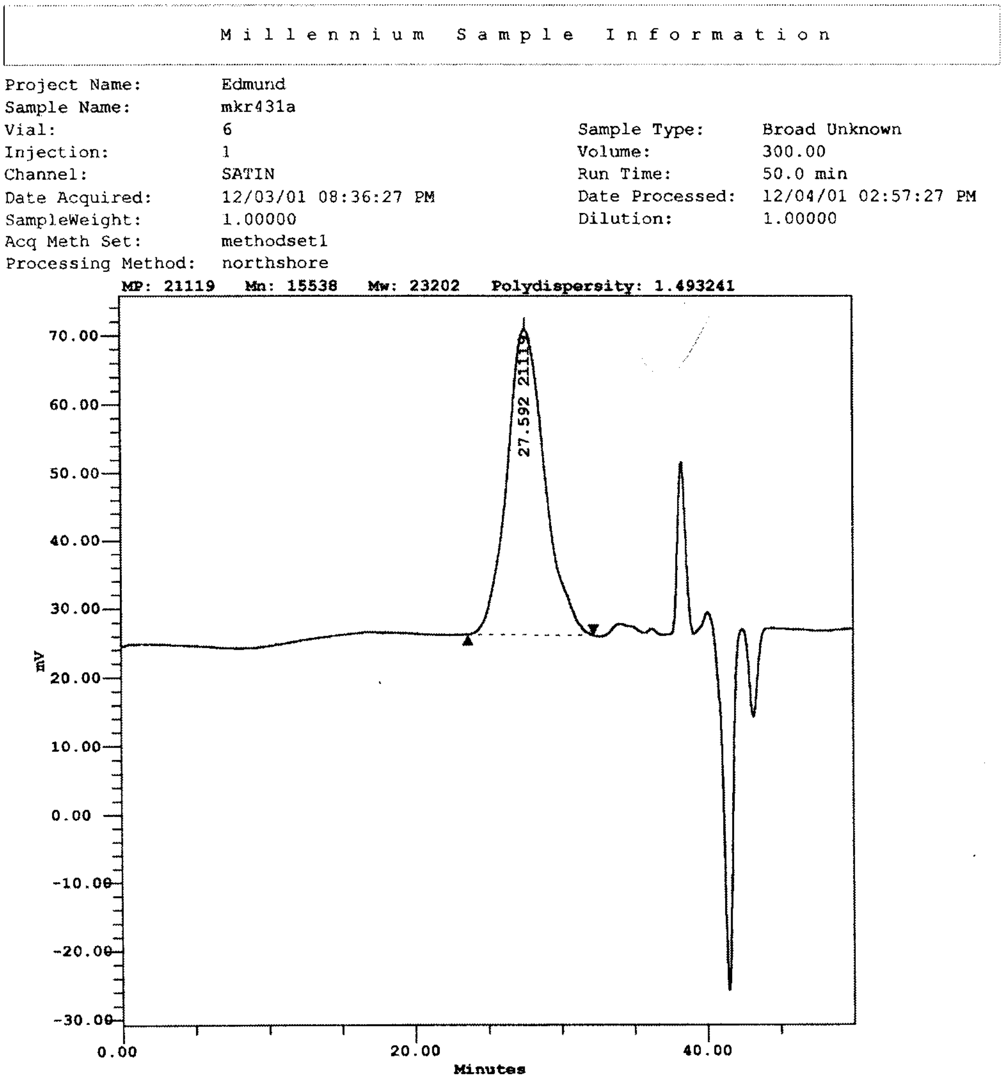


	Distribution Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		13.423	13.423	13.423	10108	15377	15874		20440	25099	1.521316	1.329243	1.632189



G4

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene] ($CDCl_3$) from 0.5 mole % AIBN for 24 hours at 75 °C in Acetonitrile



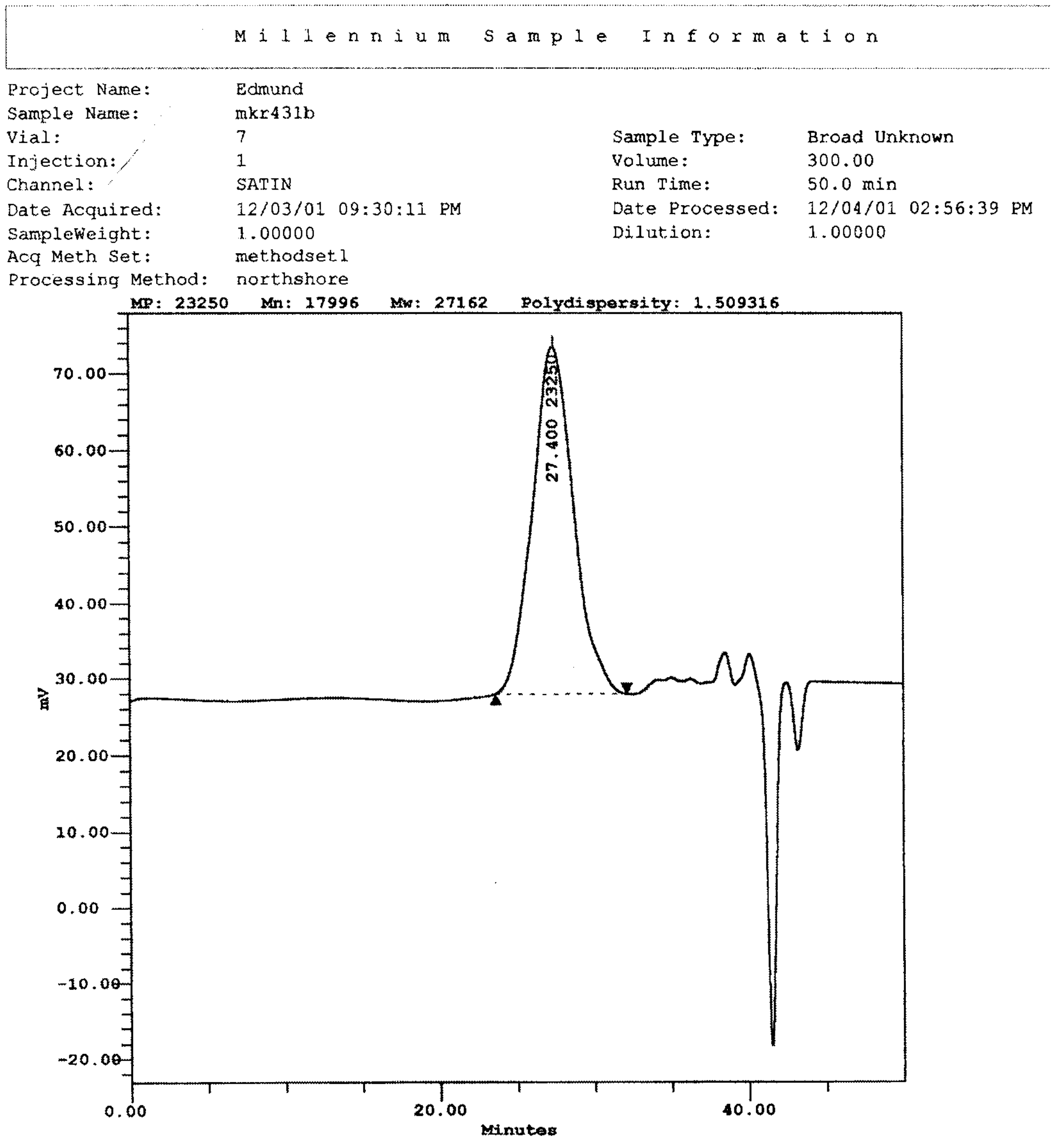
```
                    M i l l e n n i u m   S a m p l e   I n f o r m a t i o n

Project Name:         Edmund
Sample Name:          mkr431a
Vial:                 6                             Sample Type:       Broad Unknown
Injection:            1                             Volume:            300.00
Channel:              SATIN                         Run Time:          50.0 min
Date Acquired:        12/03/01 08:36:27 PM          Date Processed:    12/04/01 02:57:27 PM
SampleWeight:         1.00000                       Dilution:          1.00000
Acq Meth Set:         methodset1
Processing Method:    northshore
```

MP: 21119 Mn: 15538 Mw: 23202 Polydispersity: 1.493241

G5

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 90:10



Millennium Sample Information

Project Name: Edmund
Sample Name: mkr431b
Vial: 7
Injection: 1
Channel: SATIN
Date Acquired: 12/03/01 09:30:11 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 12/04/01 02:56:39 PM
Dilution: 1.00000

MP: 23250 Mn: 17996 Mw: 27162 Polydispersity: 1.509316

G6

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 75:25

```
                    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:        Edmund
Sample Name:         mkr431c
Vial:                8                              Sample Type:       Broad Unknown
Injection:           1                              Volume:            300.00
Channel:             SATIN                          Run Time:          50.0 min
Date Acquired:       12/03/01 10:23:55 PM           Date Processed:    12/04/01 02:56:09 PM
SampleWeight:        1.00000                        Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
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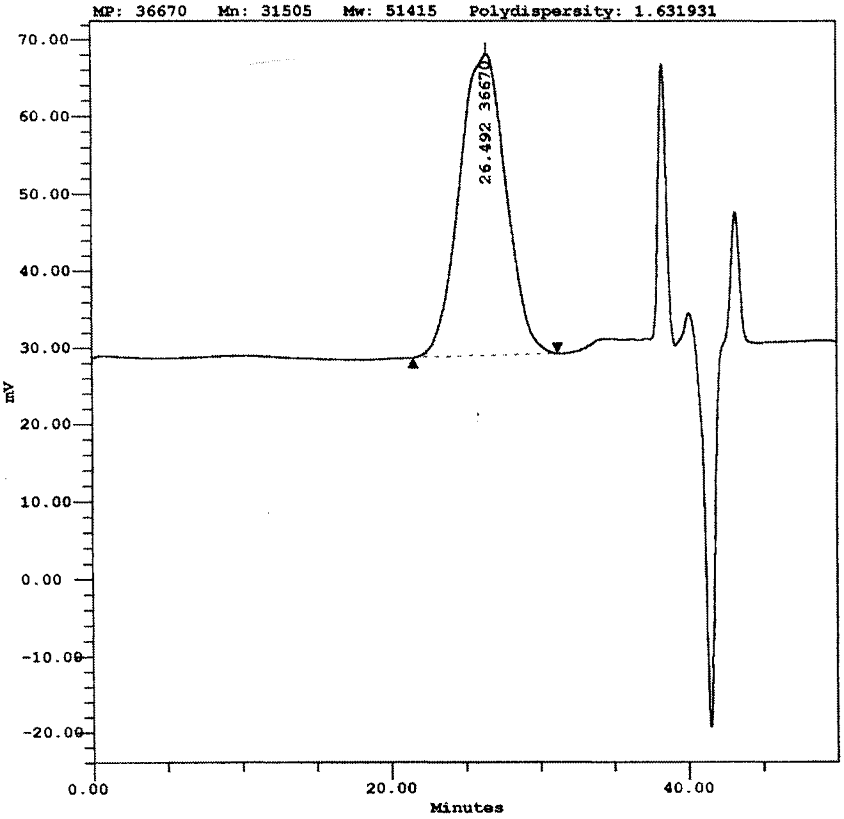
MP: 36670   Mn: 31505   Mw: 51415   Polydispersity: 1.631931



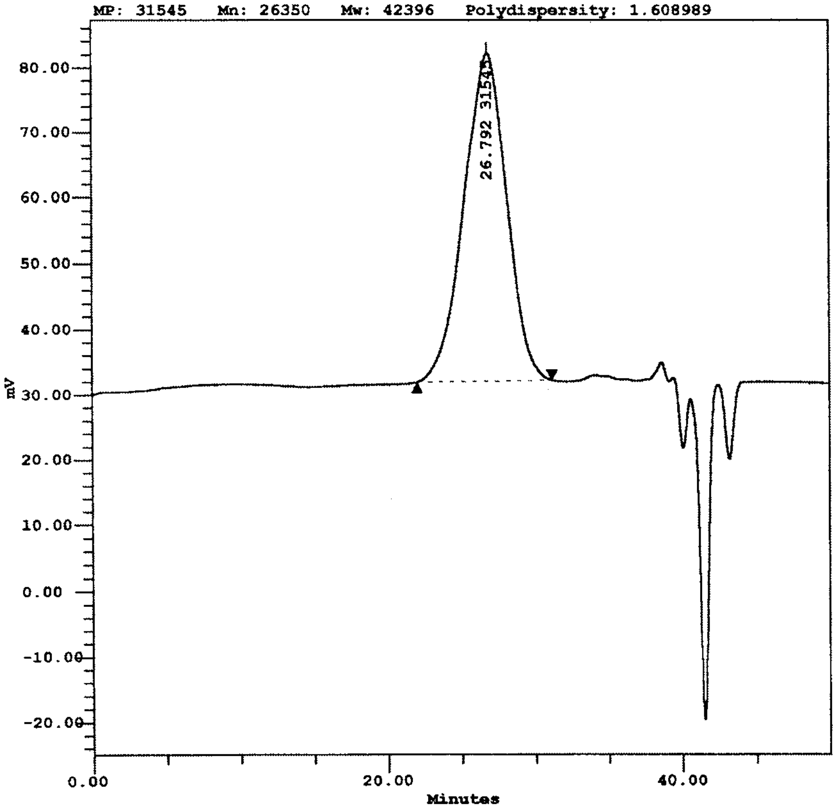
G7

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 50:50

```
                    Millennium Sample Information

Project Name:        Edmund
Sample Name:         mkr432a
Vial:                9                    Sample Type:       Broad Unknown
Injection:           1                    Volume:            300.00
Channel:             SATIN                Run Time:          50.0 min
Date Acquired:       12/03/01 11:17:39 PM Date Processed:    12/04/01 03:39:04 PM
SampleWeight:        1.00000              Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
```

MP: 31545 Mn: 26350 Mw: 42396 Polydispersity: 1.608989



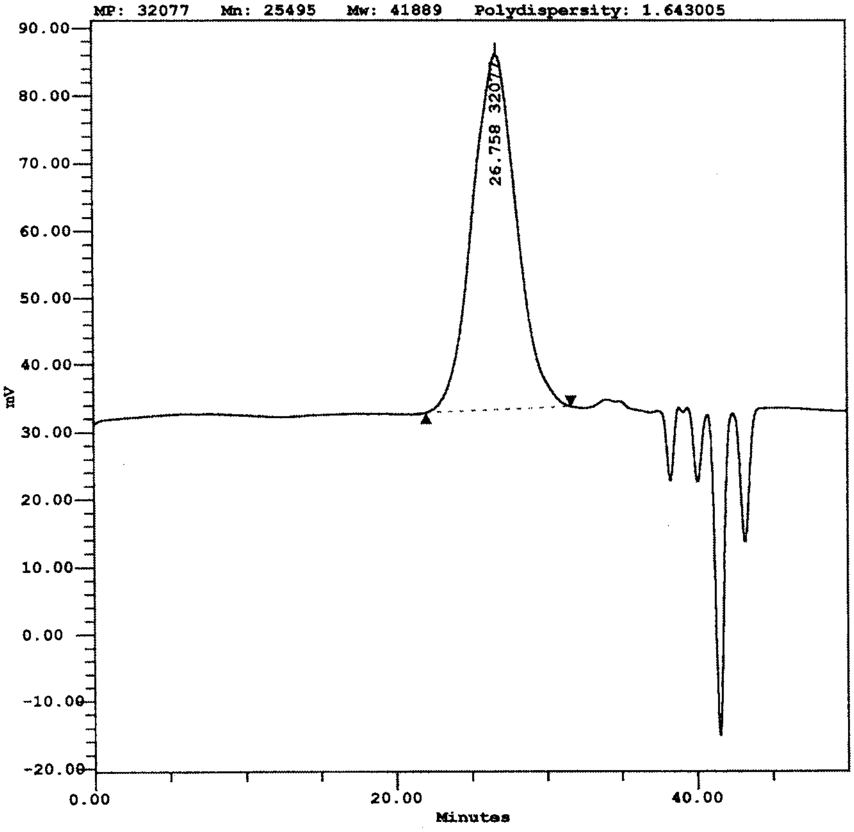
G8

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 25:75

Millennium Sample Information

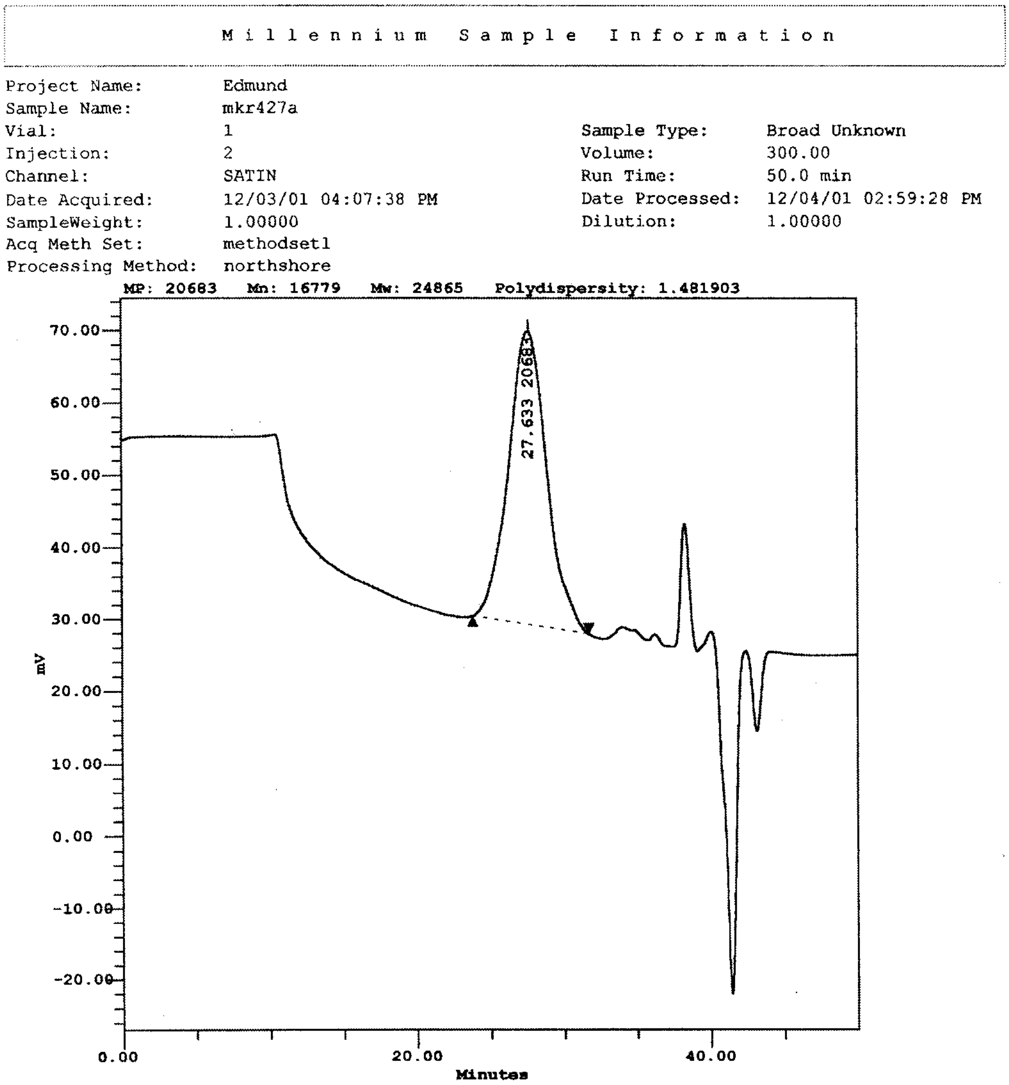
Project Name: Edmund
Sample Name: mkr432b
Vial: 10
Sample Type: Broad Unknown
Injection: 1
Volume: 300.00
Channel: SATIN
Run Time: 50.0 min
Date Acquired: 12/04/01 12:11:23 AM
Date Processed: 12/04/01 02:55:29 PM
SampleWeight: 1.00000
Dilution: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

MP: 32077 Mn: 25495 Mw: 41889 Polydispersity: 1.643005



G9

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 10:90

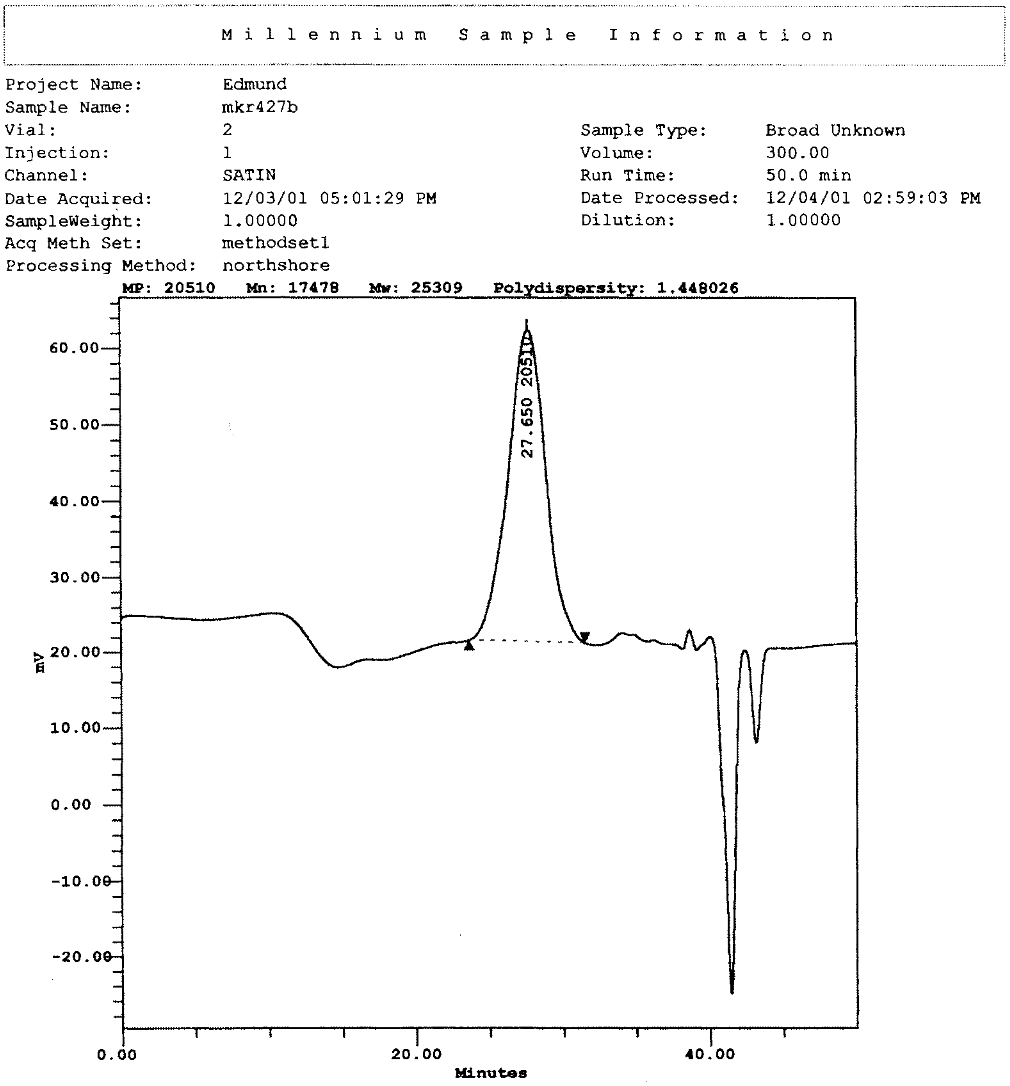


```
                    Millennium   Sample   Information

Project Name:        Edmund
Sample Name:         mkr427a
Vial:                1                          Sample Type:       Broad Unknown
Injection:           2                          Volume:            300.00
Channel:             SATIN                      Run Time:          50.0 min
Date Acquired:       12/03/01 04:07:38 PM       Date Processed:    12/04/01 02:59:28 PM
SampleWeight:        1.00000                    Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
          MP: 20683    Mn: 16779    Mw: 24865    Polydispersity: 1.481903
```

G10

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 90:10

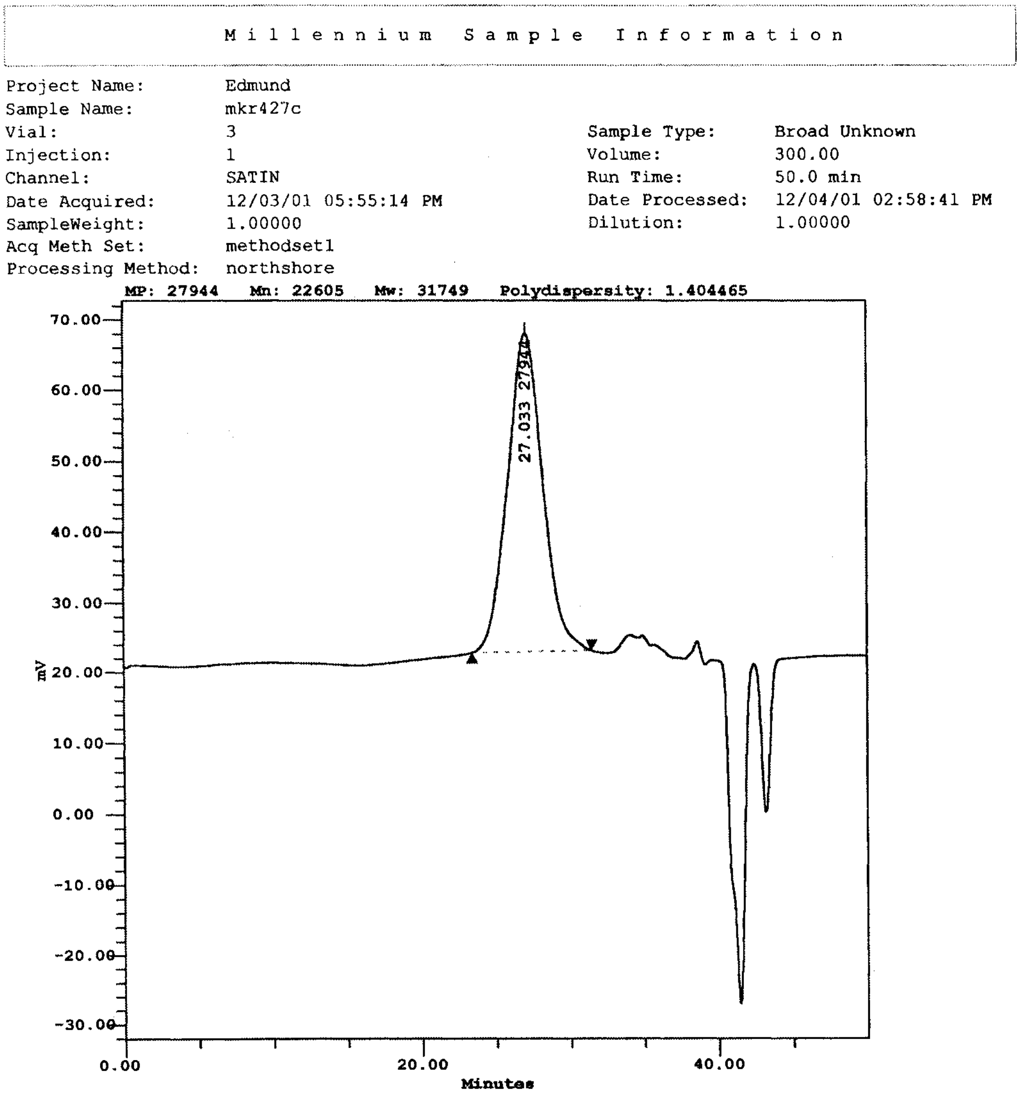


```
                  Millennium Sample Information

Project Name:        Edmund
Sample Name:         mkr427b
Vial:                2                            Sample Type:       Broad Unknown
Injection:           1                            Volume:            300.00
Channel:             SATIN                        Run Time:          50.0 min
Date Acquired:       12/03/01 05:01:29 PM         Date Processed:    12/04/01 02:59:03 PM
SampleWeight:        1.00000                      Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
          MP: 20510   Mn: 17478   Mw: 25309   Polydispersity: 1.448026
```

G11

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 75:25

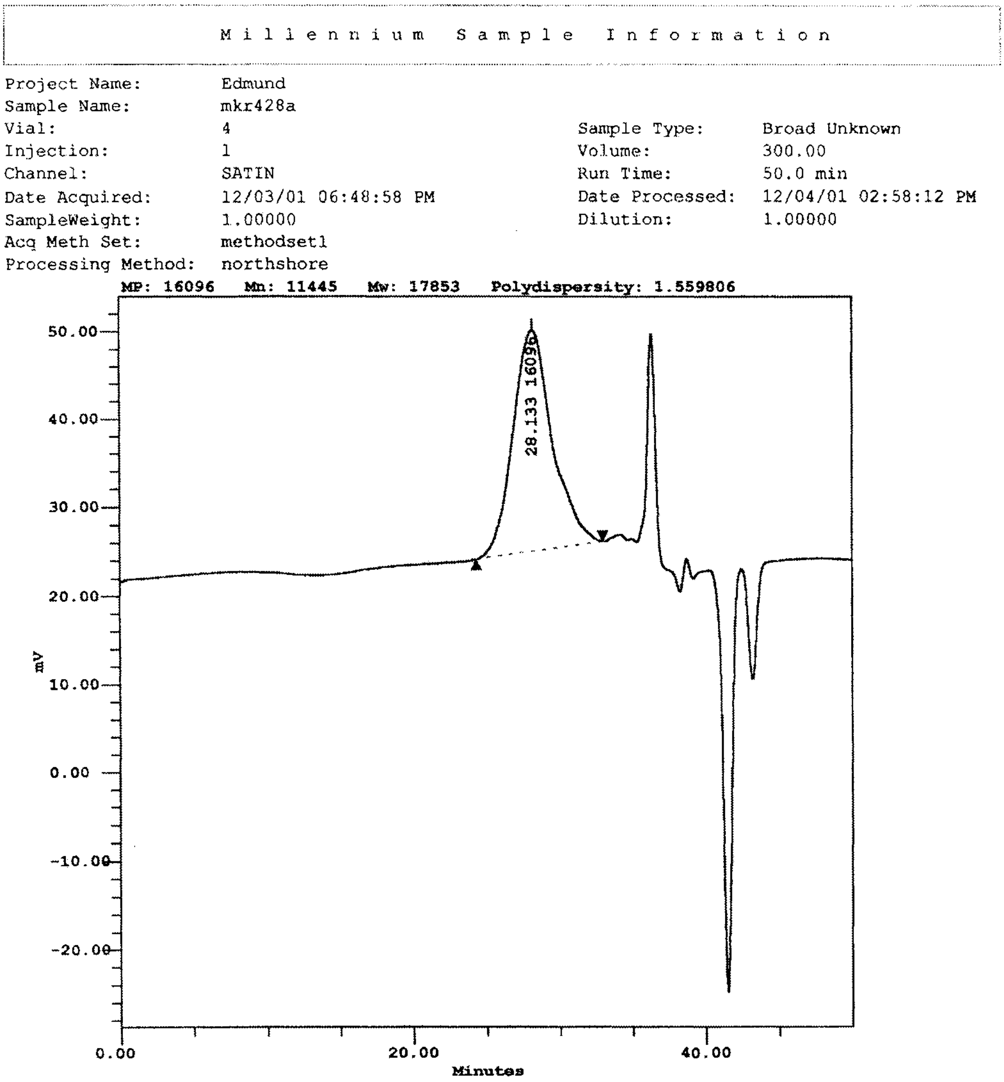


```
                    Millennium Sample Information

Project Name:       Edmund
Sample Name:        mkr427c
Vial:               3                          Sample Type:      Broad Unknown
Injection:          1                          Volume:           300.00
Channel:            SATIN                      Run Time:         50.0 min
Date Acquired:      12/03/01 05:55:14 PM       Date Processed:   12/04/01 02:58:41 PM
SampleWeight:       1.00000                    Dilution:         1.00000
Acq Meth Set:       methodset1
Processing Method:  northshore
        MP: 27944   Mn: 22605   Mw: 31749   Polydispersity: 1.404465
```

G12

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 50:50

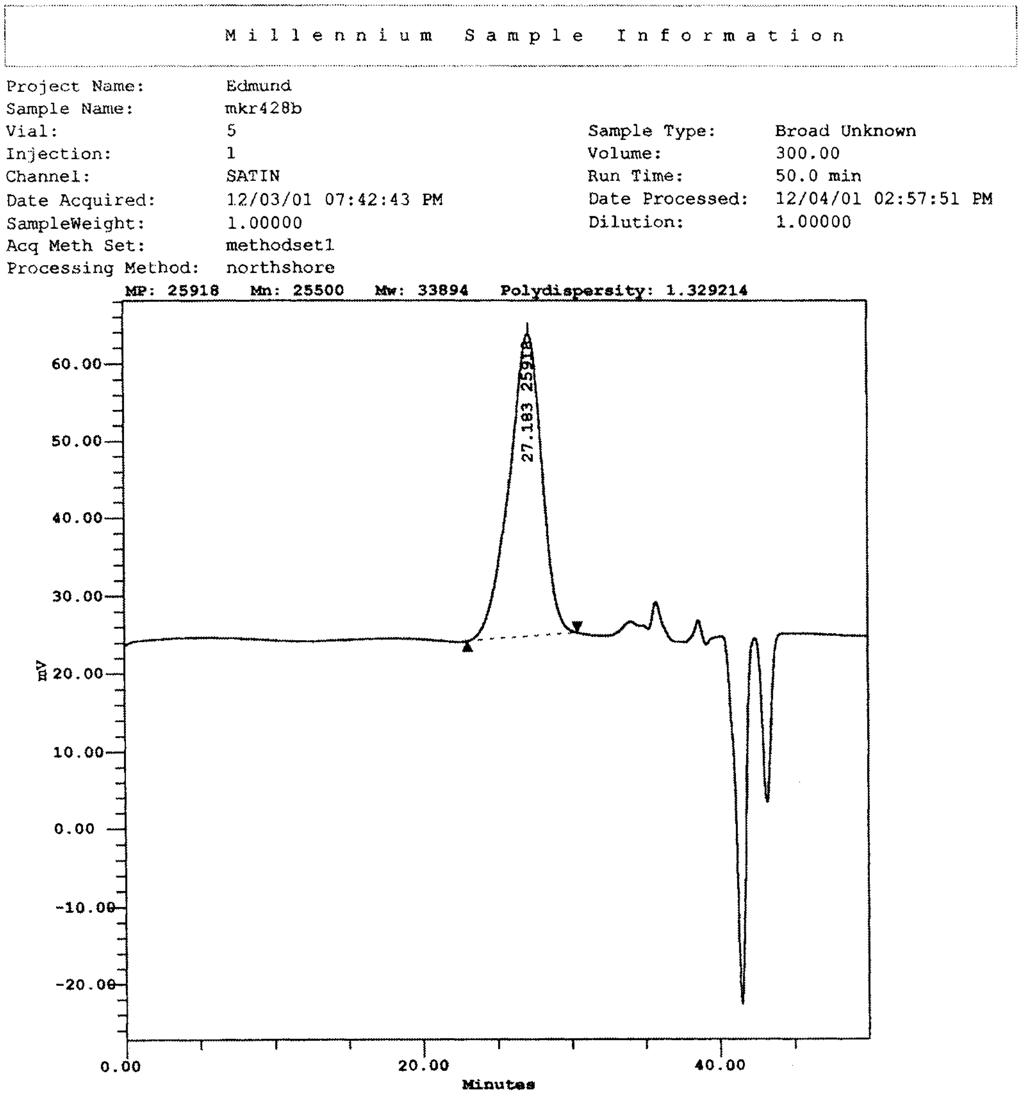


```
                  M i l l e n n i u m   S a m p l e   I n f o r m a t i o n

Project Name:        Edmund
Sample Name:         mkr428a
Vial:                4                            Sample Type:       Broad Unknown
Injection:           1                            Volume:            300.00
Channel:             SATIN                        Run Time:          50.0 min
Date Acquired:       12/03/01 06:48:58 PM         Date Processed:    12/04/01 02:58:12 PM
SampleWeight:        1.00000                      Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
      MP: 16096   Mn: 11445   Mw: 17853   Polydispersity: 1.559806
```

G13

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 25:75

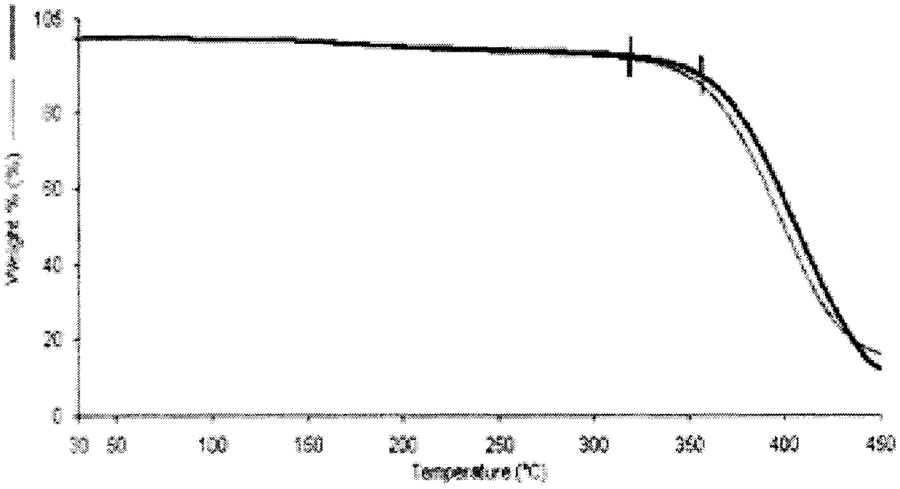


```
                    M i l l e n n i u m   S a m p l e   I n f o r m a t i o n

Project Name:         Edmund
Sample Name:          mkr428b
Vial:                 5                           Sample Type:      Broad Unknown
Injection:            1                           Volume:           300.00
Channel:              SATIN                       Run Time:         50.0 min
Date Acquired:        12/03/01 07:42:43 PM        Date Processed:   12/04/01 02:57:51 PM
SampleWeight:         1.00000                     Dilution:         1.00000
Acq Meth Set:         methodset1
Processing Method:    northshore
        MP: 25918   Mn: 25500   Mw: 33894   Polydispersity: 1.329214
```

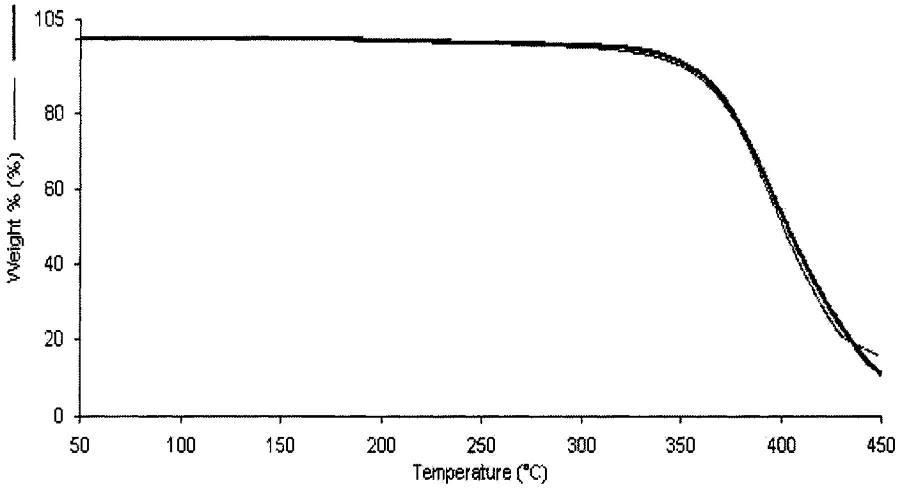
G14

GPC of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 10:90



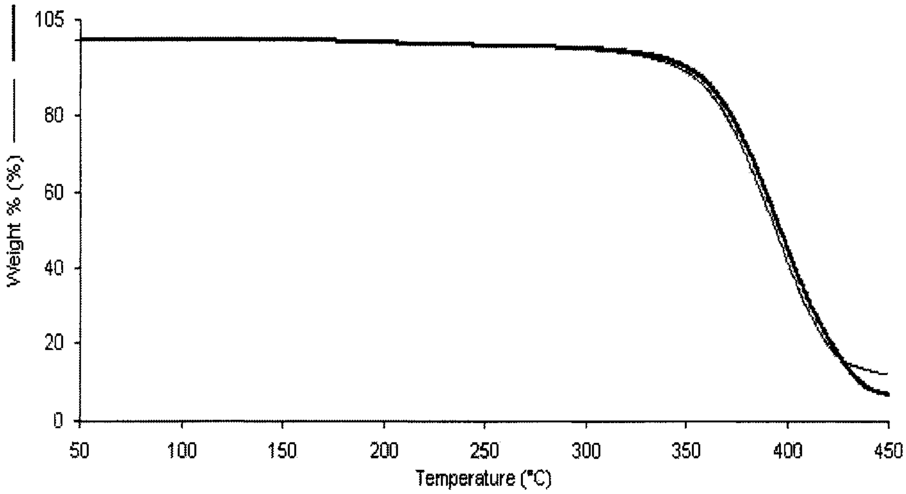
TGA1

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene]



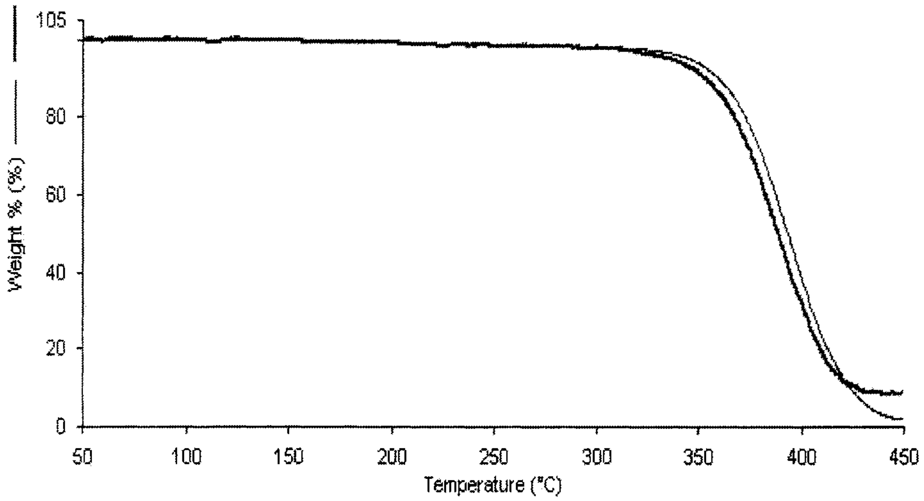
TGA2

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 90:10



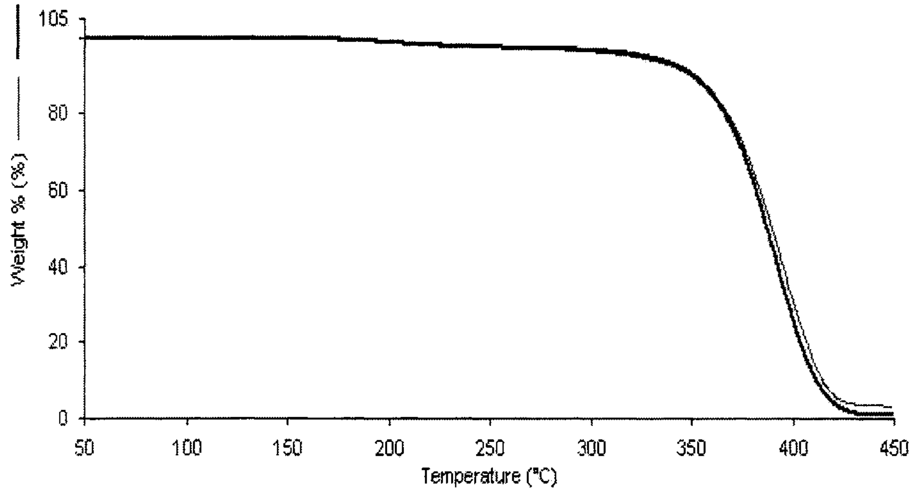
TGA3

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 75:25



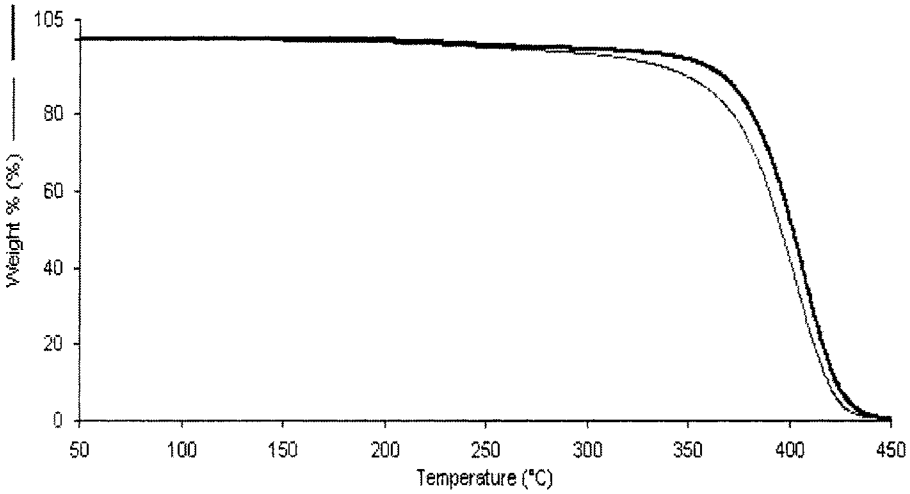
TGA4

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 50:50



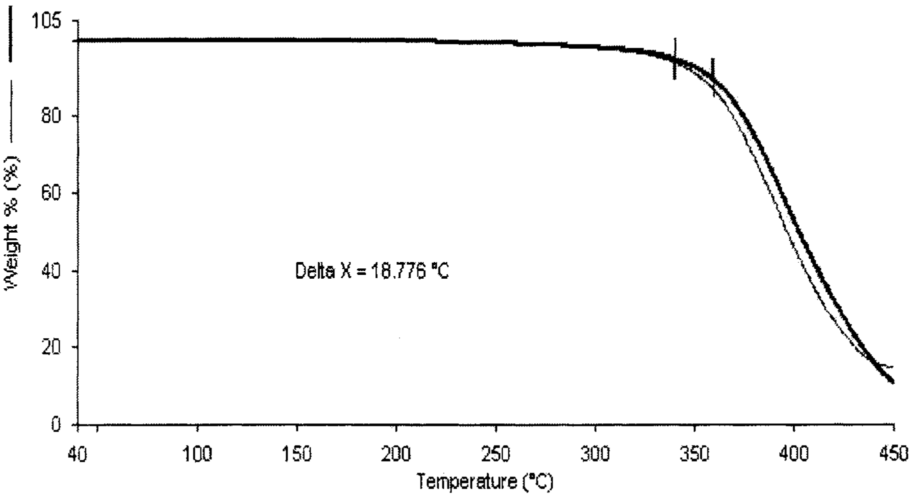
TGA5

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 25:75



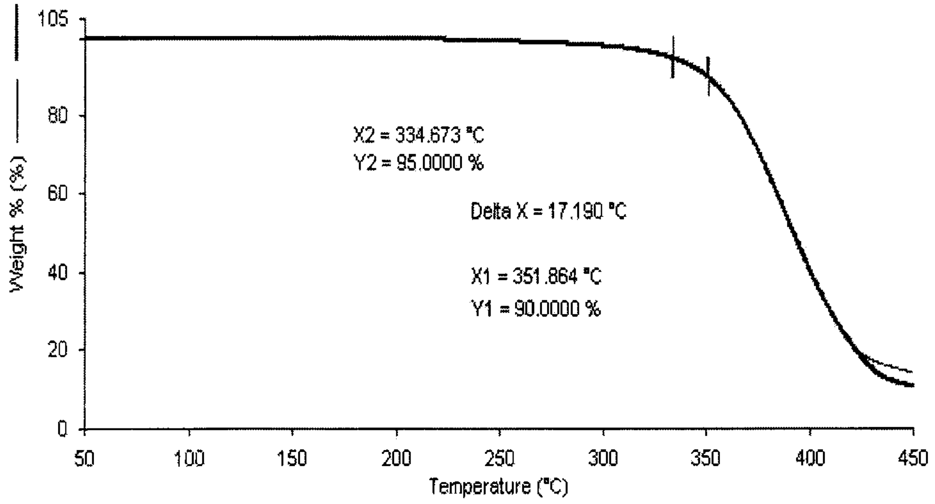
TGA6

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 10:90



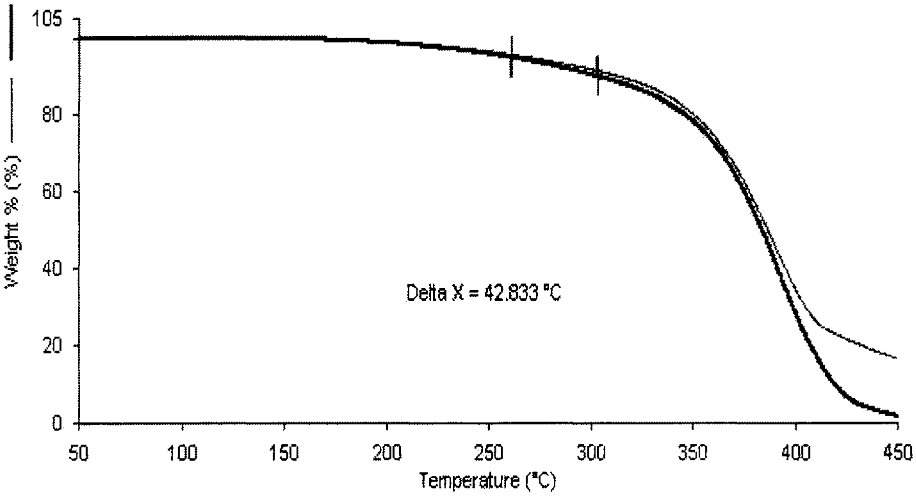
TGA7

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 90:10



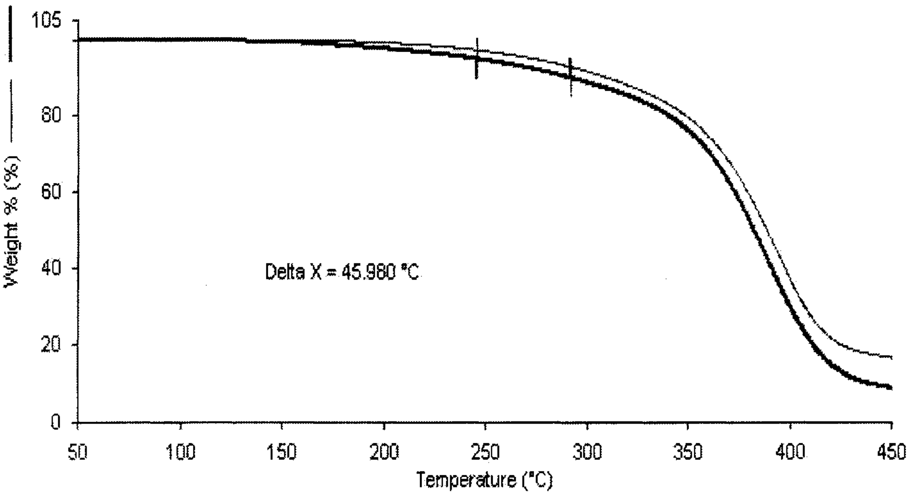
TGA8

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 75:25



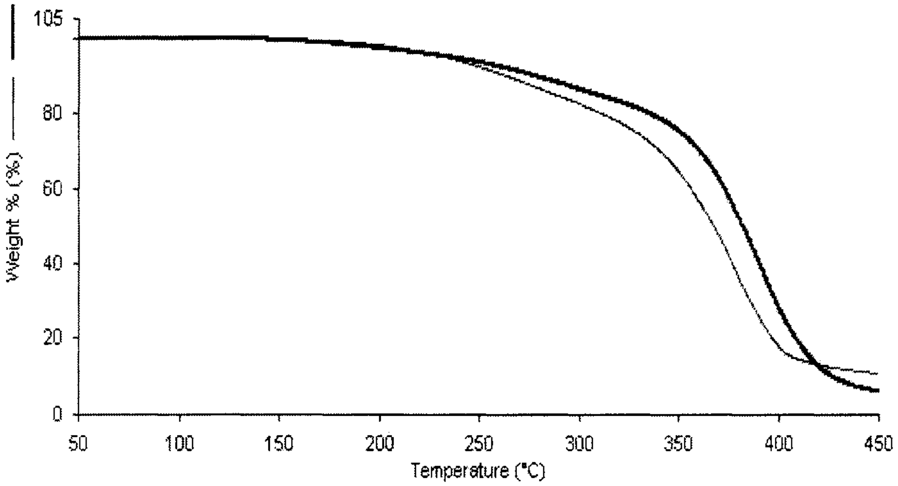
TGA9

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 50:50



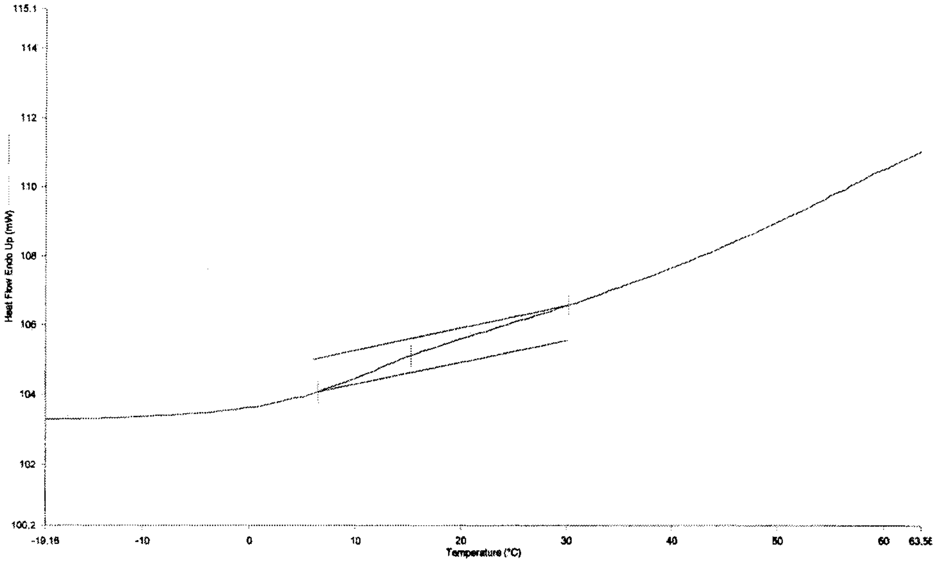
TGA10

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 25:75



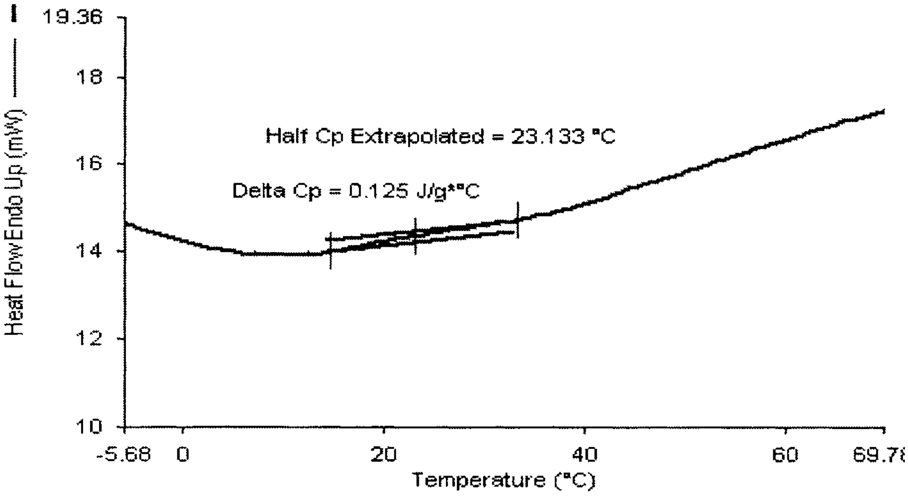
TGA11

TGA of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 10:90



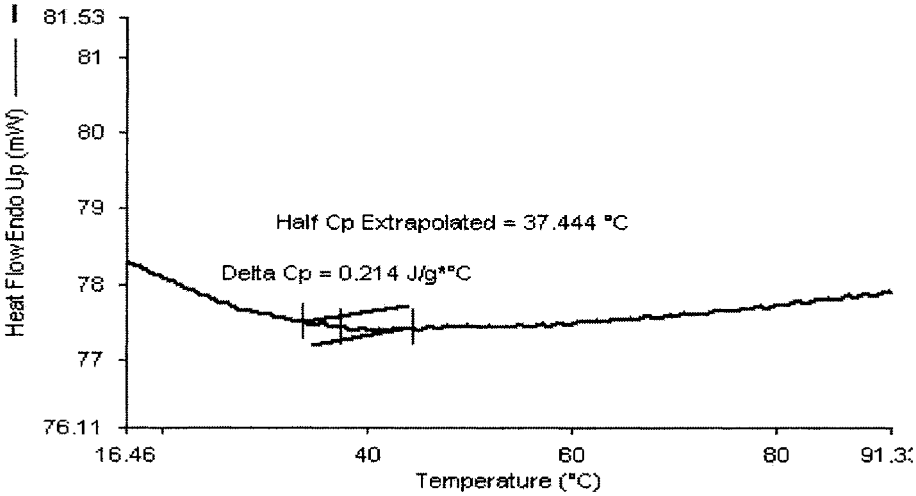
D1

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene]



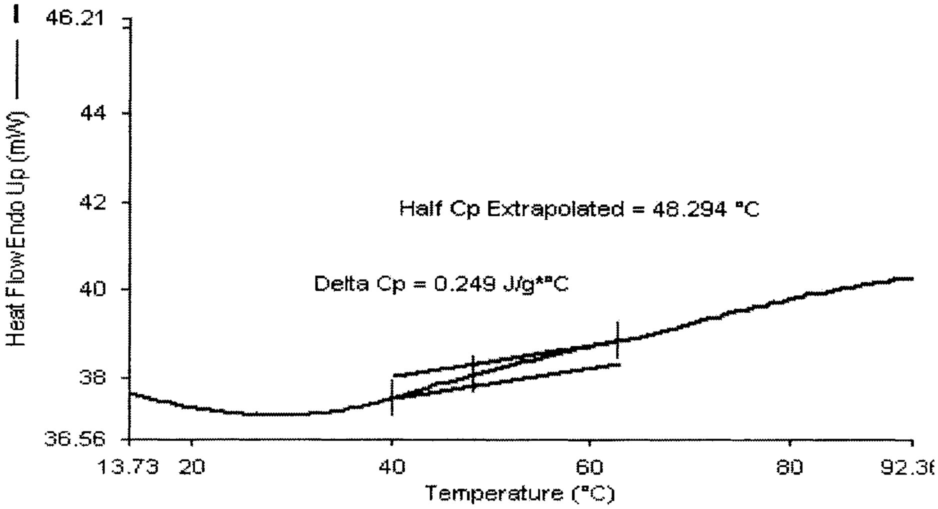
D2

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 90:10



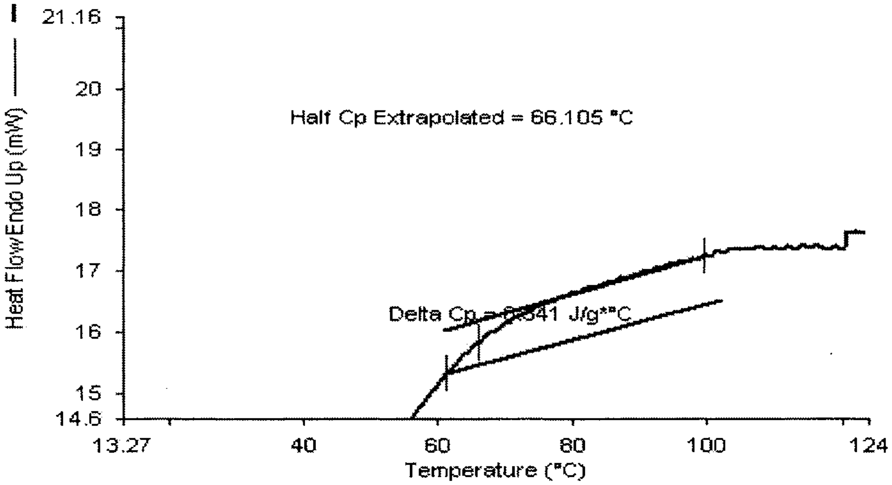
D3

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 75:25



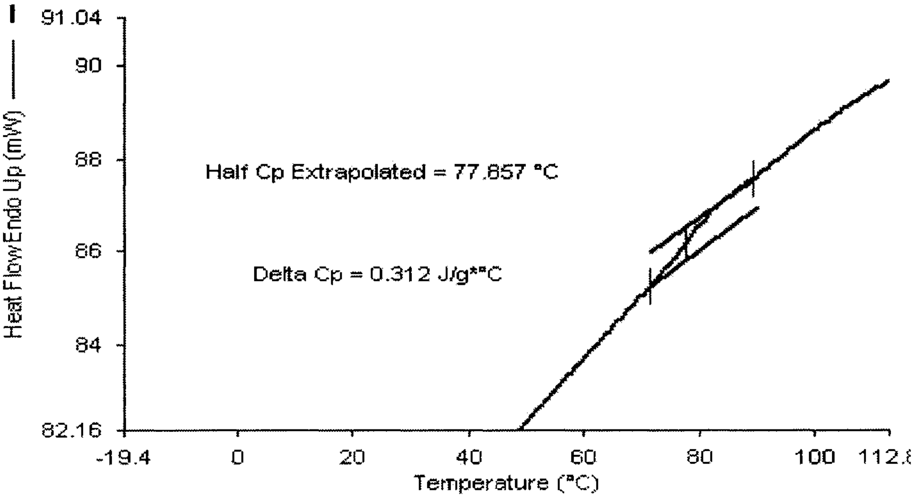
D4

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 50:50



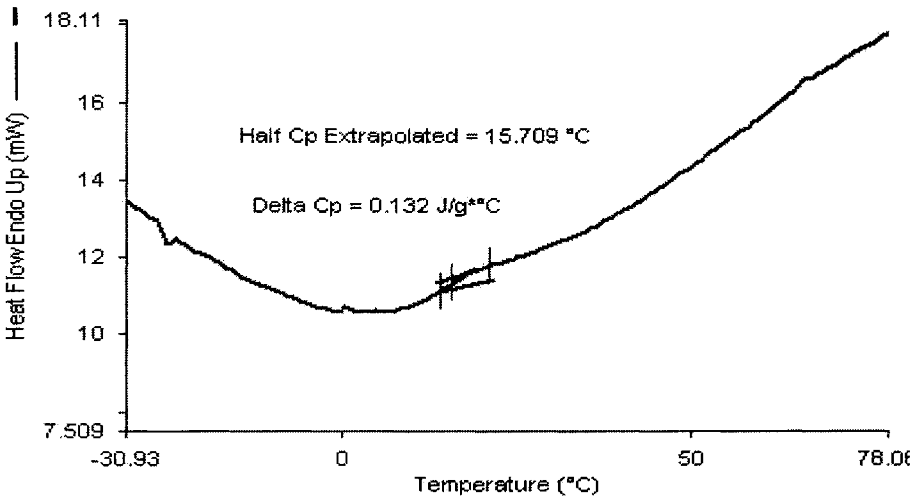
D5

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 25:75



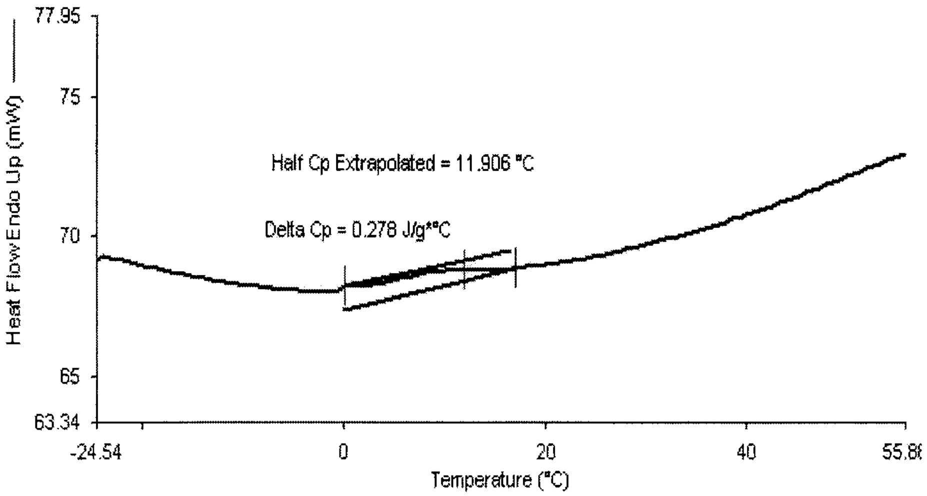
D6

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 10:90



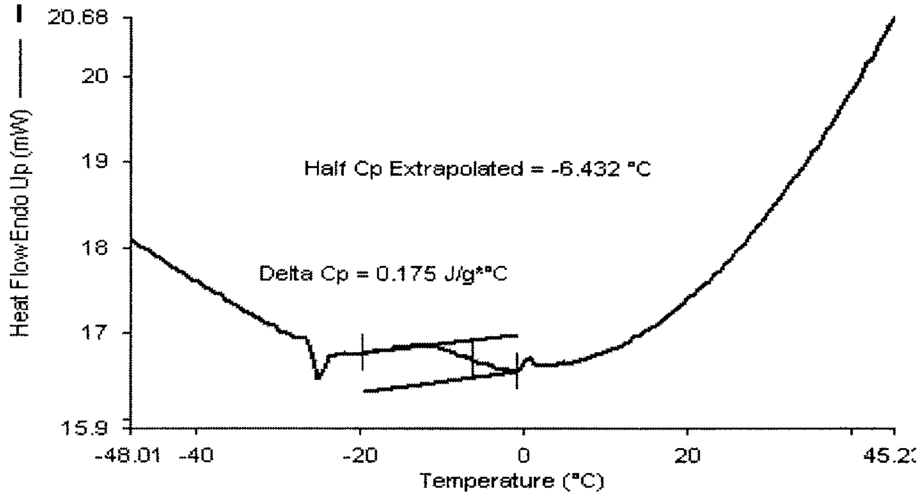
D7

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 90:10



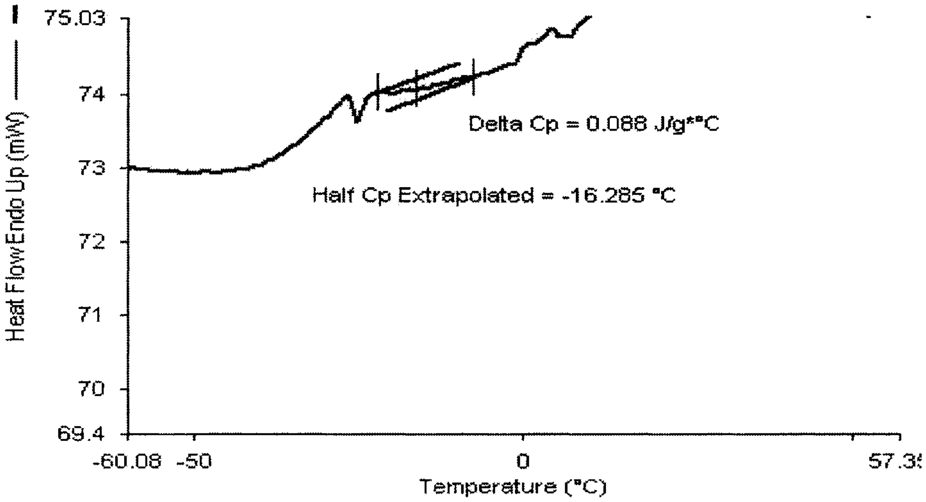
D8

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 75:25



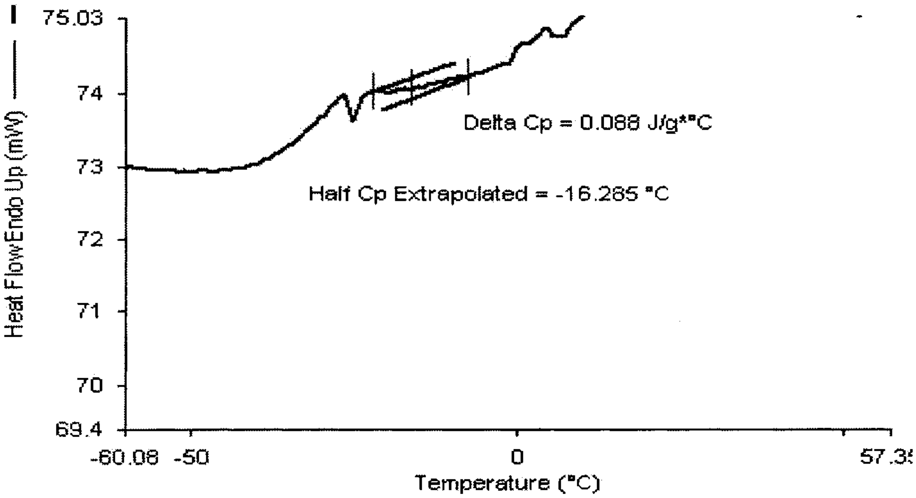
D9

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 50:50



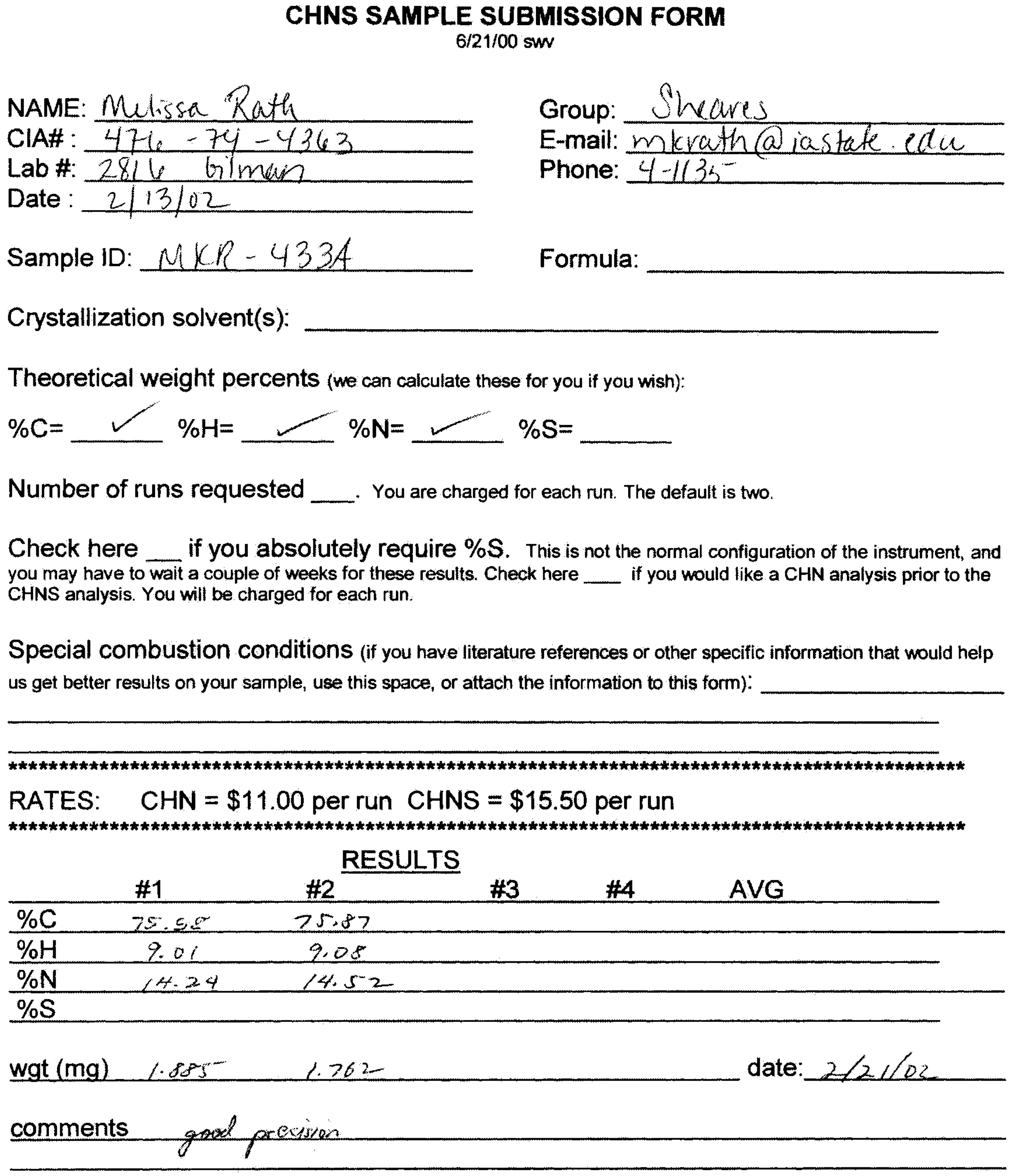
D10

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 25:75



D11

DSC data for Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 10:90



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Rath
Group: Sheares
CIA# : 476-79-4363
E-mail: mkrath@iastate.edu
Lab #: 2816 Gilman
Phone: 4-1135
Date : 2/13/02

Sample ID: MKR-433A
Formula:

Crystallization solvent(s):

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S=

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form):

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

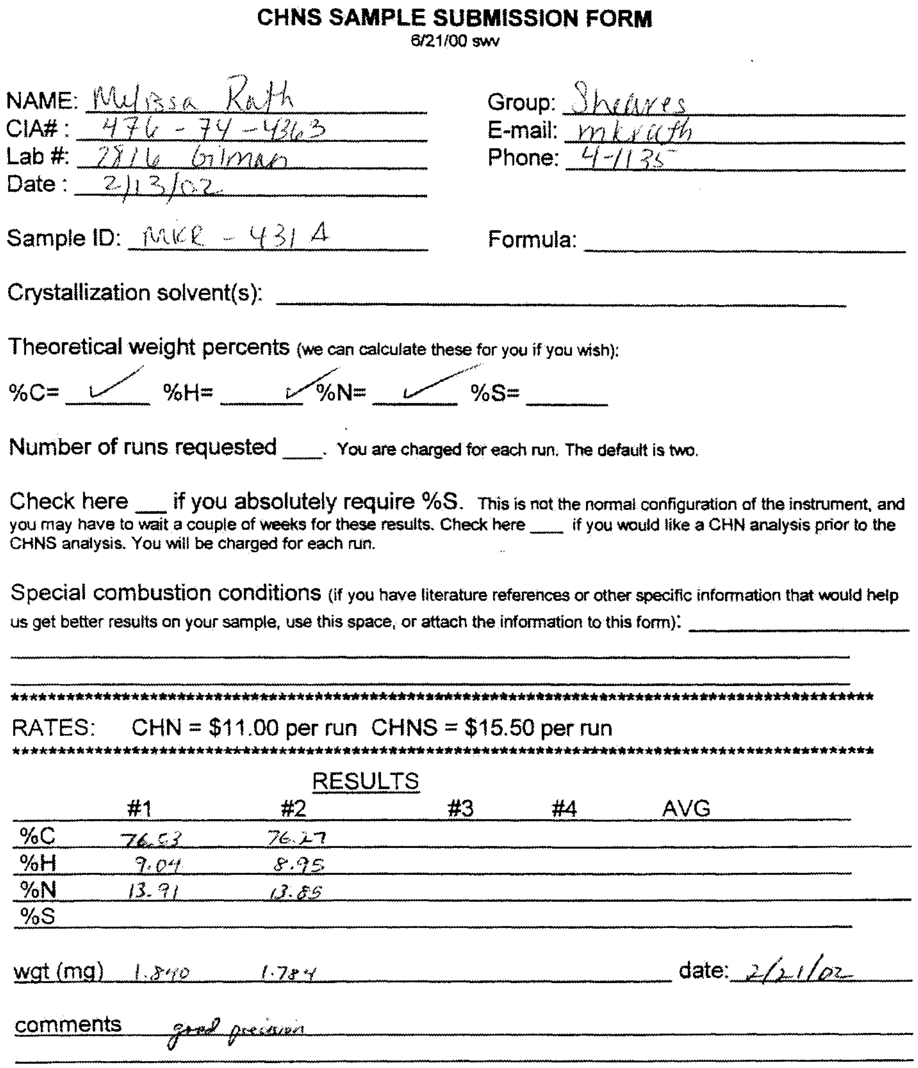
	#1	#2	#3	#4	AVG
%C	75.55	75.87			
%H	9.01	9.08			
%N	14.24	14.52			
%S					

wgt (mg) 1.885 1.762 date: 2/21/02

comments good precision

EA1

Elemental Analysis for Poly[2,3-bis(cyanopropyl)-1,3-butadiene]



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Rath
CIA# : 476 - 74 - 4363
Lab #: 2816 Gilman
Date : 2/13/02

Group: Shears
E-mail: mkrath
Phone: 4-1135

Sample ID: MKR - 431 A

Formula: ____

Crystallization solvent(s): ____

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ____

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ____

RATES: CHN = $11.00 per run CHNS = $15.50 per run

RESULTS

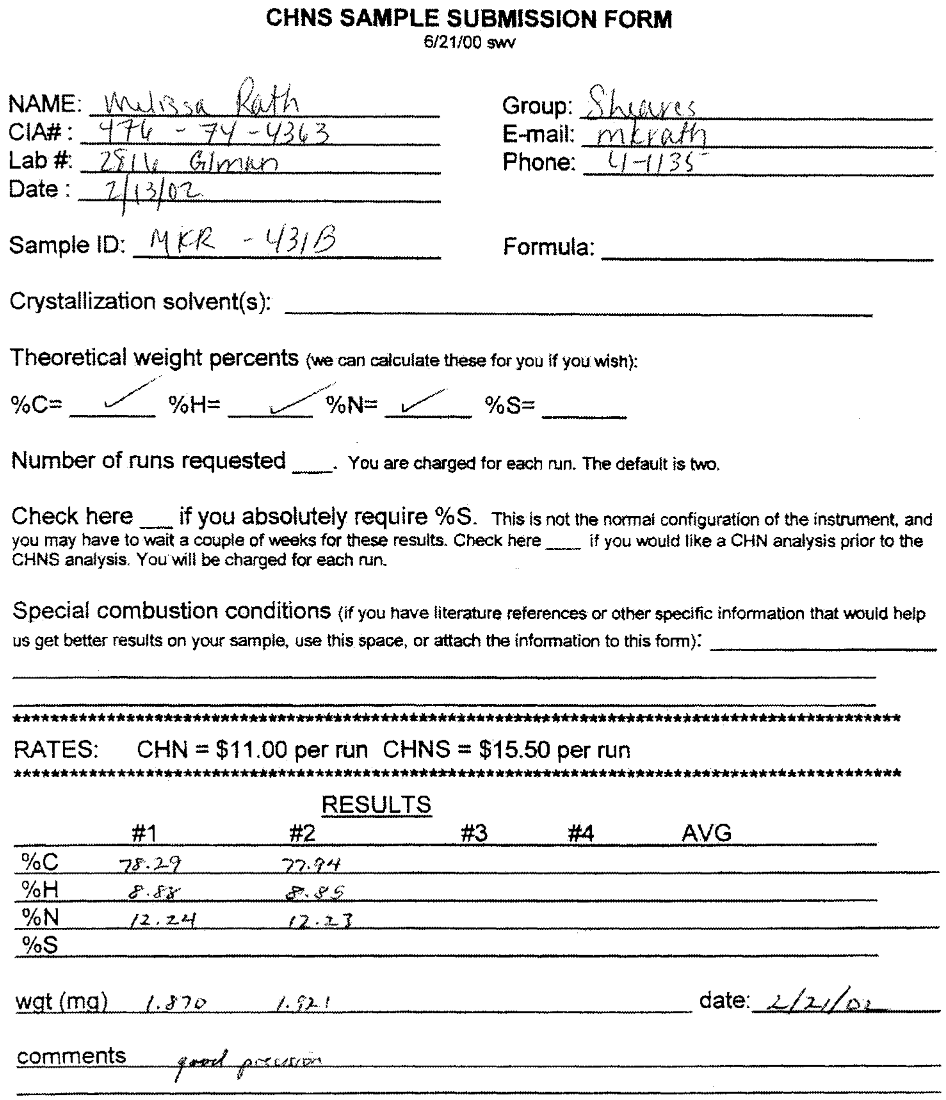
	#1	#2	#3	#4	AVG
%C	76.53	76.27			
%H	9.04	8.95			
%N	13.91	13.85			
%S					

wgt (mg) 1.840 1.784 date: 2/21/02

comments good precision

EA2

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 90:10



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Rath
CIA# : 476 - 74 - 4363
Lab #: 2816 Gilman
Date : 2/13/02

Group: Sheares
E-mail: mkrath
Phone: 4-1135

Sample ID: MKR - 431B

Formula: ______

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

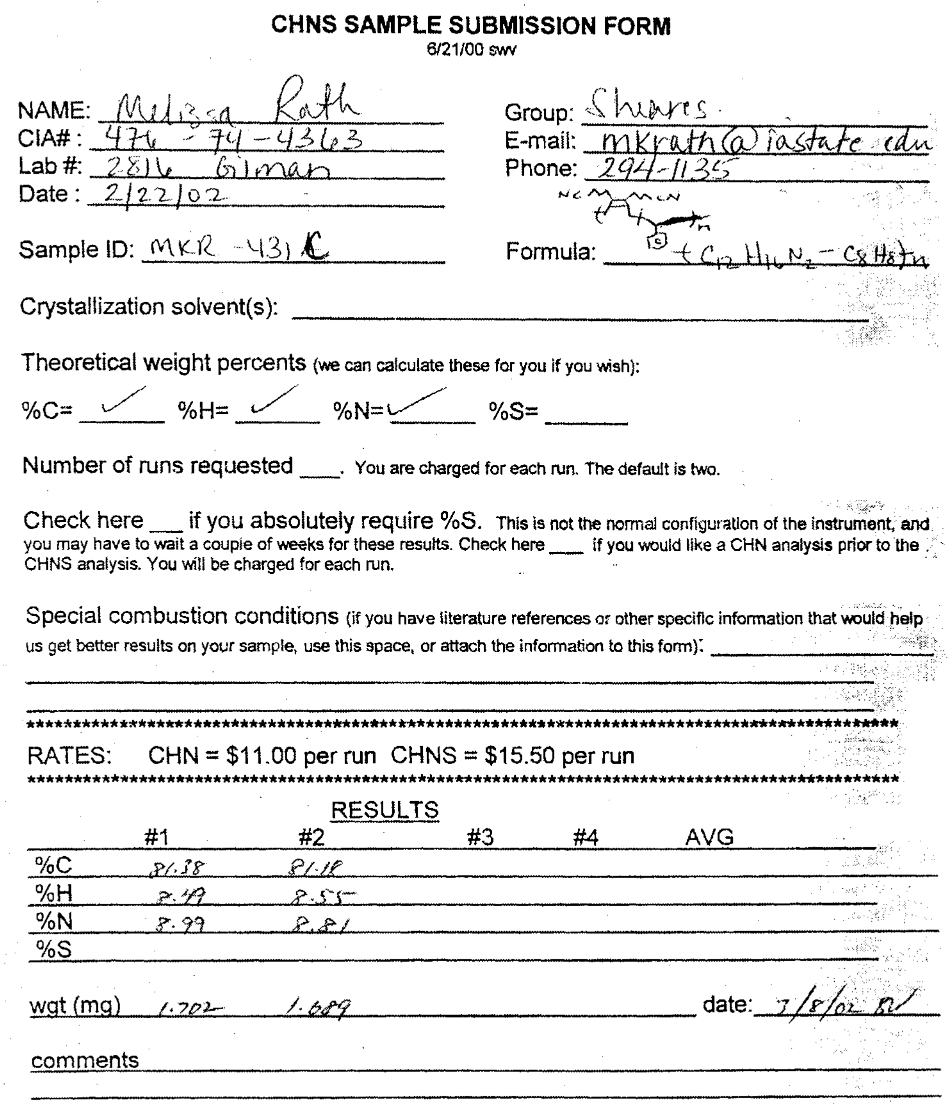
	#1	#2	#3	#4	AVG
%C	78.29	77.94			
%H	8.88	8.85			
%N	12.24	12.23			
%S					

wgt (mg) 1.870 1.921 date: 2/21/02

comments good precision

EA 3

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 75:25



CHNS SAMPLE SUBMISSION FORM
6/21/00 swv

NAME: Melissa Rath
CIA#: 476 - 74 - 4363
Lab #: 2816 Gilman
Date: 2/22/02

Group: Shinars
E-mail: mkrath@iastate.edu
Phone: 294-1135

Sample ID: MKR -431 C

Formula: $(C_{12}H_{16}N_2-C_8H_8)_n$

Crystallization solvent(s): ________

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ____

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ________

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

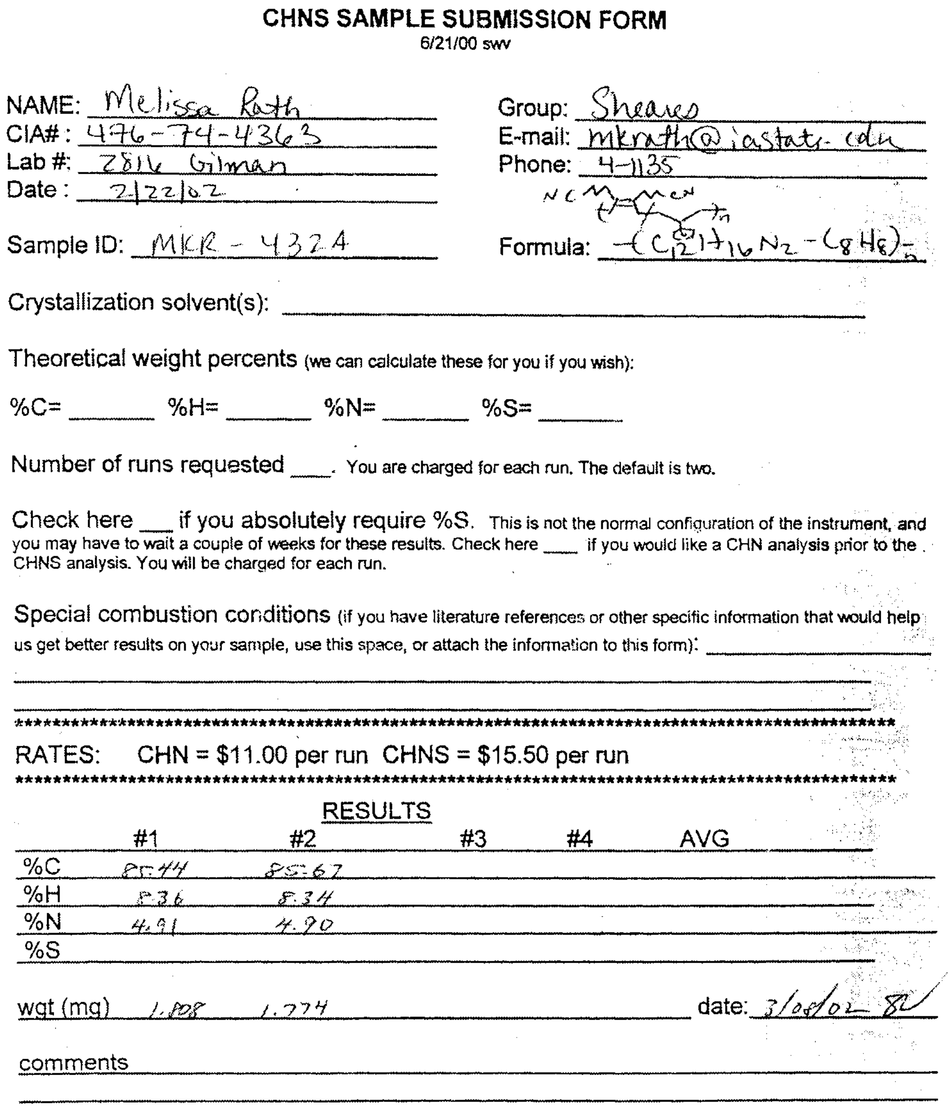
	#1	#2	#3	#4	AVG
%C	81.38	81.18			
%H	8.49	8.55			
%N	8.99	8.81			
%S					

wgt (mg) 1.702 1.689 date: 7/8/02

comments

EA 4

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 50:50



CHNS SAMPLE SUBMISSION FORM
6/21/00 swv

NAME: Melissa Roth
CIA# : 476-74-4363
Lab #: 2816 Gilman
Date : 2/22/02

Group: Sheares
E-mail: mkrath@iastate.edu
Phone: 4-1135

Sample ID: MKR - 4324
Formula: $-(C_{12}H_{16}N_2-C_8H_8)-_n$

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ______ %H= ______ %N= ______ %S= ______

Number of runs requested ___. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ___ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

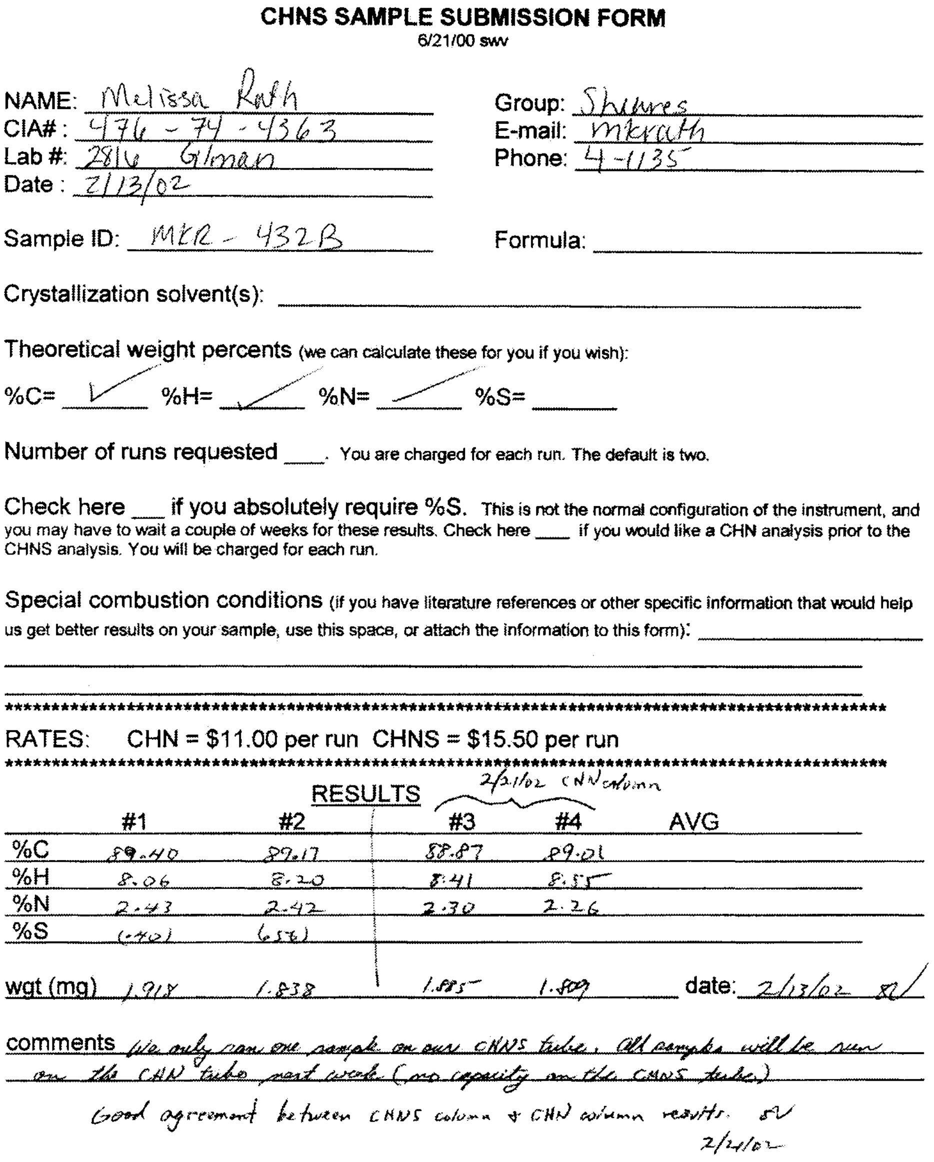
	#1	#2	#3	#4	AVG
%C	85.44	85.67			
%H	8.36	8.34			
%N	4.91	4.90			
%S					

wgt (mg) 1.808 1.774 date: 3/08/02 SV

comments ______

EA 5

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 25:75



CHNS SAMPLE SUBMISSION FORM
6/21/00 swv

NAME: Melissa Roth
CIA# : 476 - 74 - 4363
Lab #: 2816 Gilman
Date : 2/13/02

Group: Shinnes
E-mail: mkrath
Phone: 4-1135

Sample ID: MKR - 432B

Formula: ______

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

2/21/02 CHN column

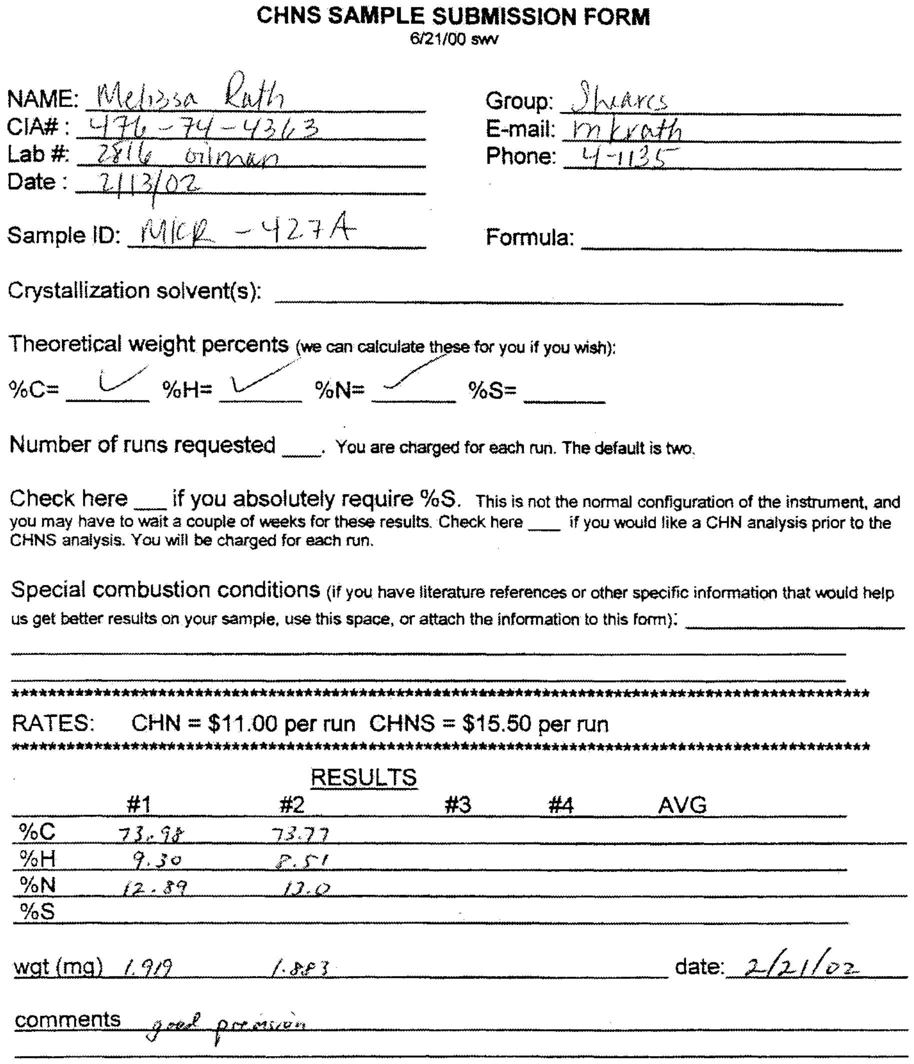
	#1	#2	#3	#4	AVG
%C	89.40	89.17	88.87	89.01	
%H	8.06	8.20	8.41	8.55	
%N	2.43	2.42	2.30	2.26	
%S	(.40)	(.56)			
wgt (mg)	1.918	1.838	1.885	1.809	date: 2/13/02 SV

comments We only ran one sample on our CHNS tube. All samples will be run on the CHN tube next week (no capacity on the CHNS tube)

Good agreement between CHNS column & CHN column results. SV
2/21/02

EA6

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-styrene] from feed ratio 10:90



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Roth

Group: Shears

CIA# : 476-74-4363

E-mail: mkroth

Lab #: 2816 Gilman

Phone: 4-1135

Date : 2/13/02

Sample ID: MKR -427A

Formula: ______

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ___ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

	#1	#2	#3	#4	AVG
%C	73.98	73.77			
%H	9.30	8.51			
%N	12.89	12.0			
%S					

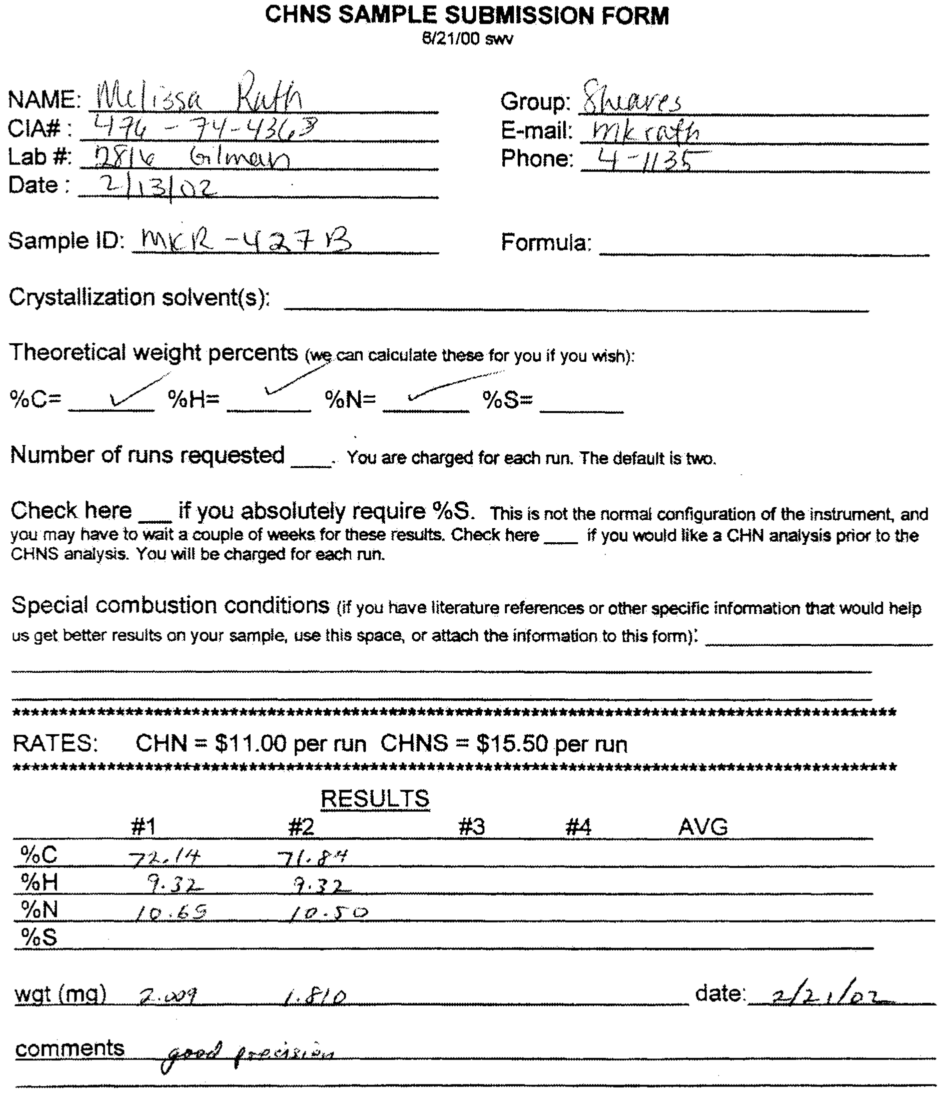
wgt (mg) 1.919 1.883

date: 2/21/02

comments good precision

EA7

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 90:10



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Roth
CIA# : 476 - 74-4363
Lab #: 2816 Gilman
Date : 2/13/02

Group: Sheares
E-mail: mkroth
Phone: 4-1135

Sample ID: MKR-427B

Formula: ______

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

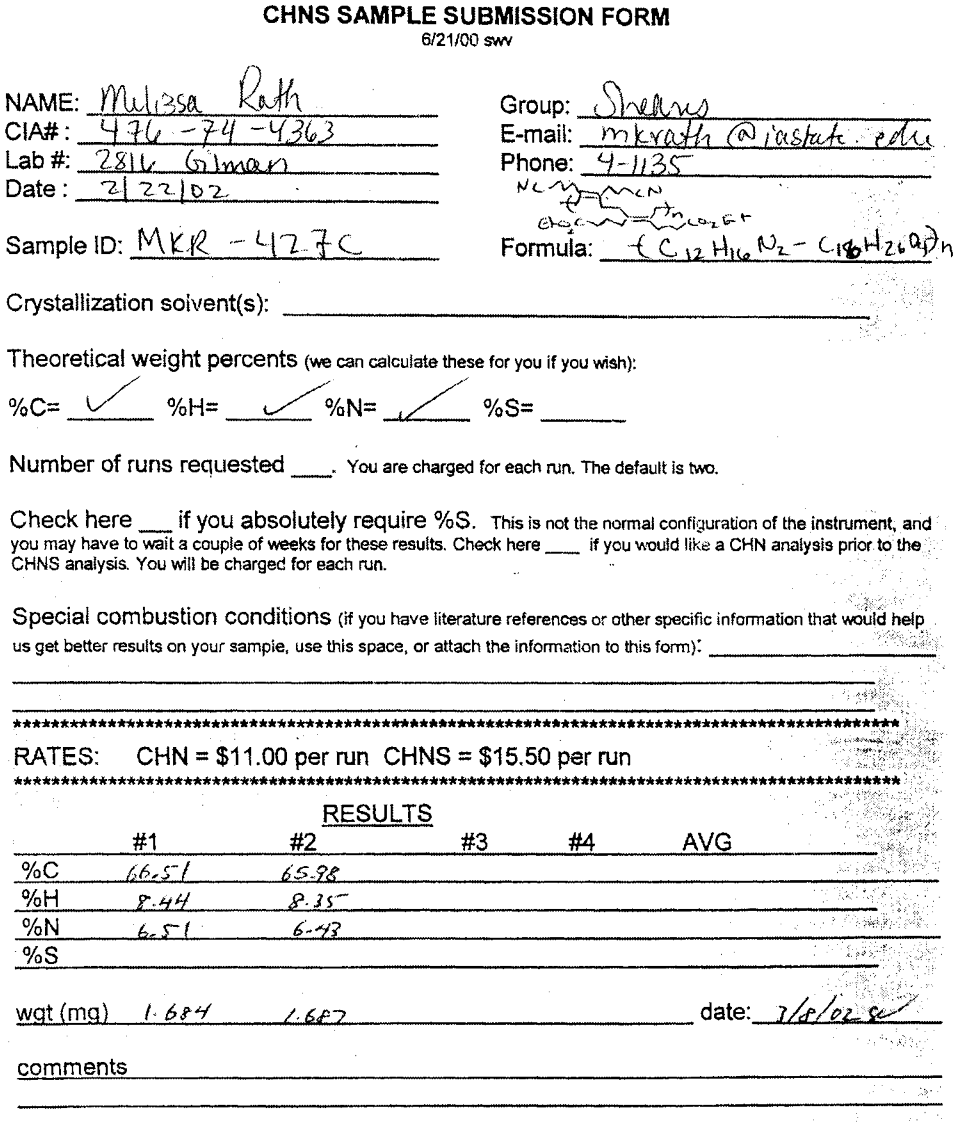
	#1	#2	#3	#4	AVG
%C	72.14	71.84			
%H	9.32	9.32			
%N	10.65	10.50			
%S					

wgt (mg) 2.009 1.810 date: 2/21/02

comments good precision

EA8

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 75:25



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Rath
CIA#: 476-74-4363
Lab #: 2816 Gilman
Date: 2/22/02

Group: Shears
E-mail: mkrath@iastate.edu
Phone: 4-1135

Sample ID: MKR-427C

Formula: $-(C_{12}H_{16}N_2 - C_{16}H_{26}O_4)_n$

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

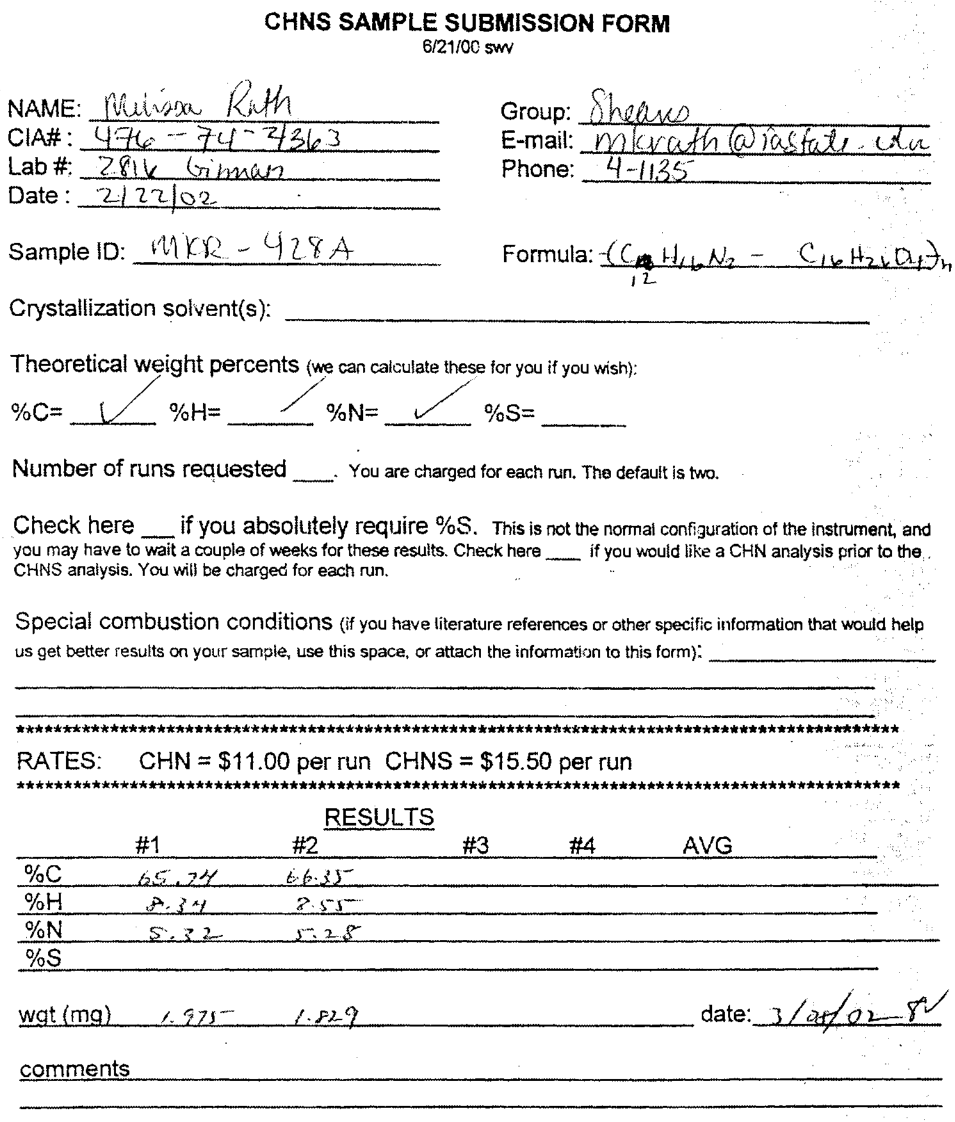
	#1	#2	#3	#4	AVG
%C	66.51	65.98			
%H	8.44	8.35			
%N	6.51	6.43			
%S					

wgt (mg) 1.684 1.687 date: 3/8/02

comments ______

EA9

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 50:50



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Rath

CIA#: 476-74-7363

Lab #: 2816 Gilman

Date: 2/22/02

Group: Shears

E-mail: mkrath@iastate.edu

Phone: 4-1135

Sample ID: MKR-428A

Formula: $-(C_{12}H_{16}N_2 - C_{16}H_{26}O_4)_n$

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ✓ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

* * *

RATES: CHN = \$11.00 per run CHNS = \$15.50 per run

* * *

RESULTS

	#1	#2	#3	#4	AVG
%C	65.74	66.35			
%H	8.34	8.55			
%N	5.32	5.28			
%S					

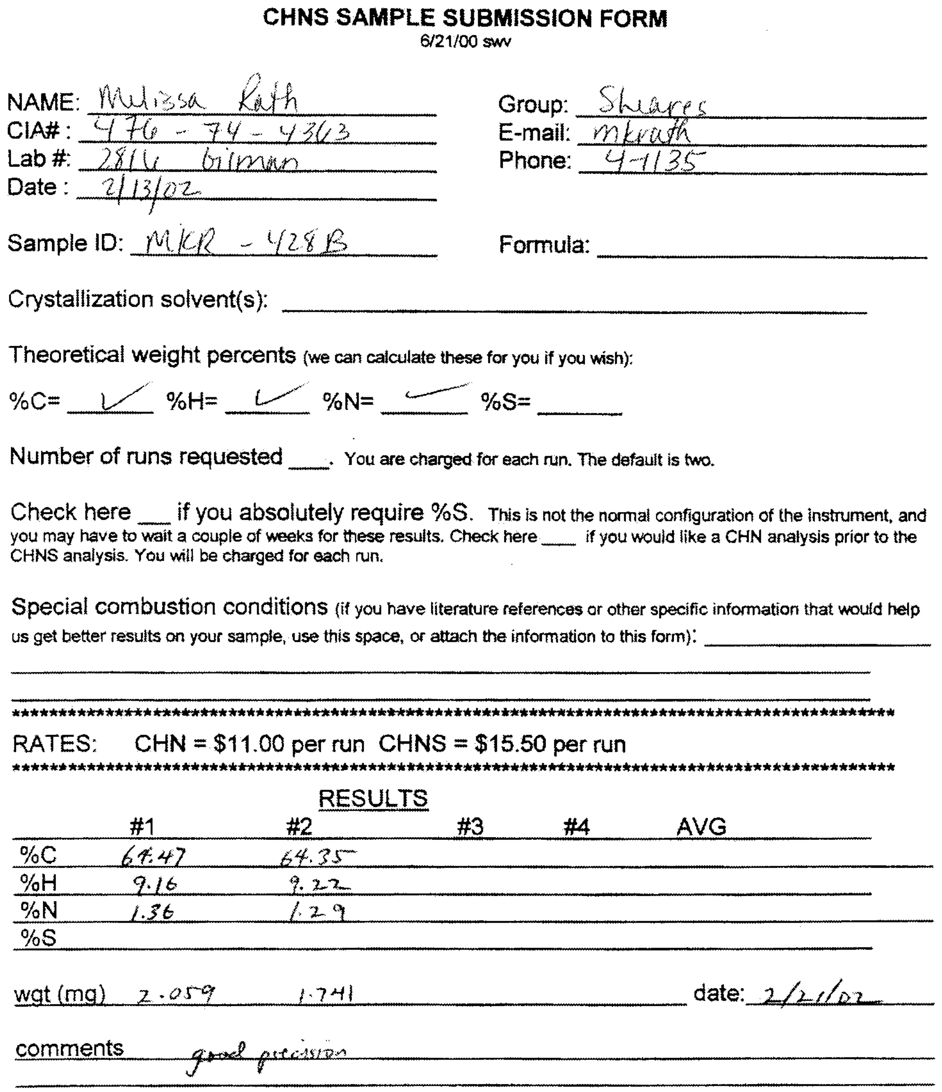
wgt (mg) 1.975 1.829

date: 3/04/02

comments ______

EA10

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 25:75



CHNS SAMPLE SUBMISSION FORM
6/21/00 swv

NAME: Melissa Rath
CIA# : 476 - 74 - 4363
Lab # : 2816 Gilman
Date : 2/13/02

Group: Shares
E-mail: mkrath
Phone: 4-1135

Sample ID: MKR - 428B

Formula: ______

Crystallization solvent(s): ______

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ______ %S= ______

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ______

****

RATES: CHN = $11.00 per run CHNS = $15.50 per run

****

RESULTS

	#1	#2	#3	#4	AVG
%C	64.47	64.35			
%H	9.16	9.22			
%N	1.36	1.29			
%S					

wgt (mg) 2.059 1.741 date: 2/21/02

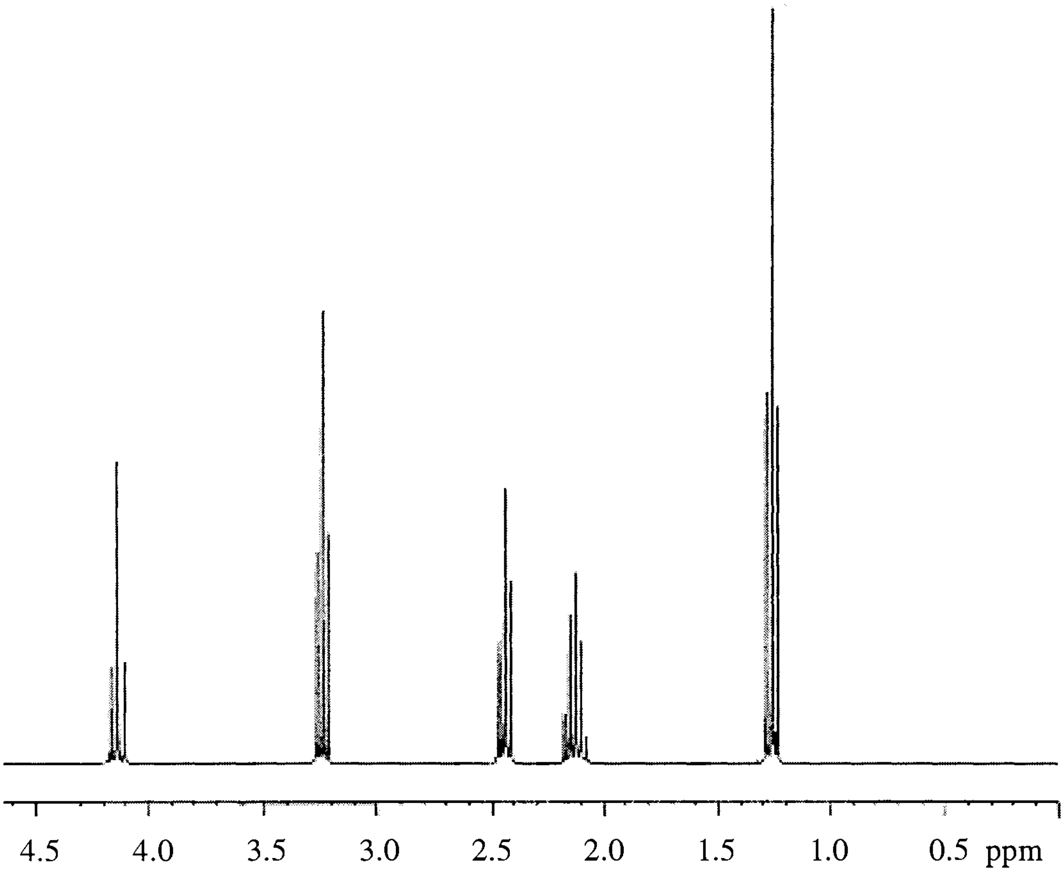
comments good precision

EA11

Elemental Analysis of Poly[2,3-bis(cyanopropyl)-1,3-butadiene-*co*-2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene] from feed ratio 10:90

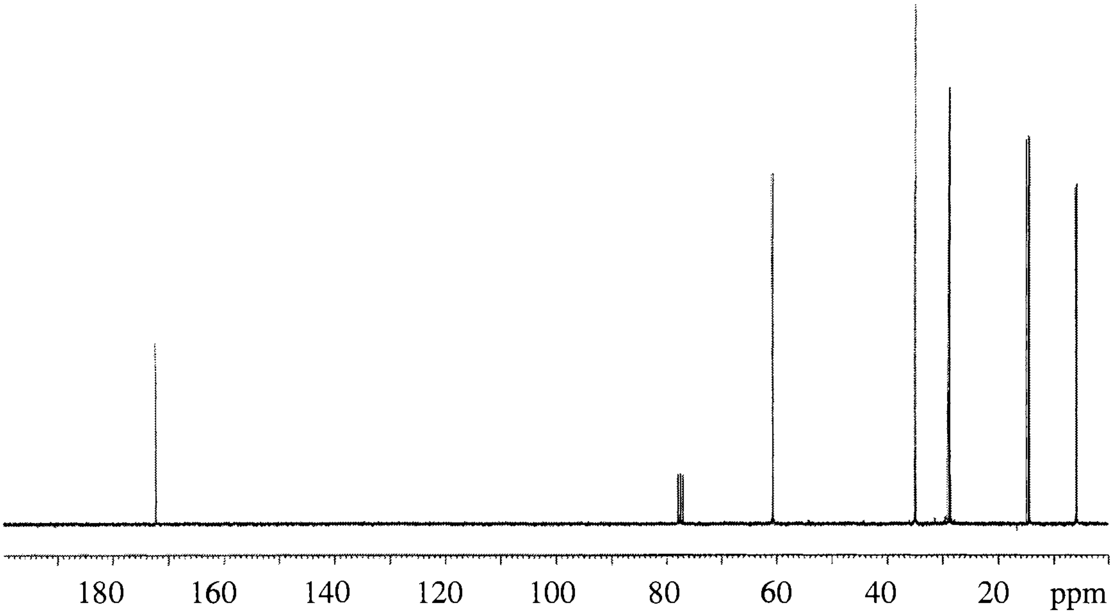
APPENDIX B:

Chapter 2. Data



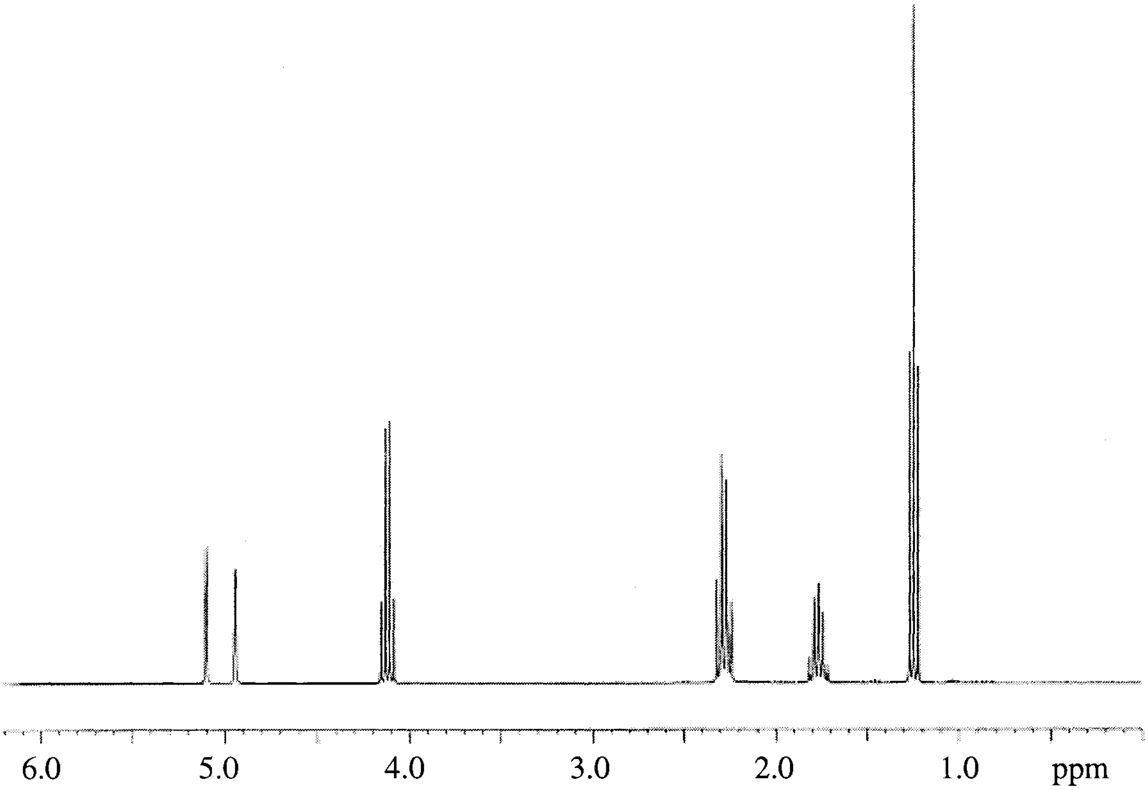
N8

Ethyl δ-iodobutyrate ($CDCl_3$)



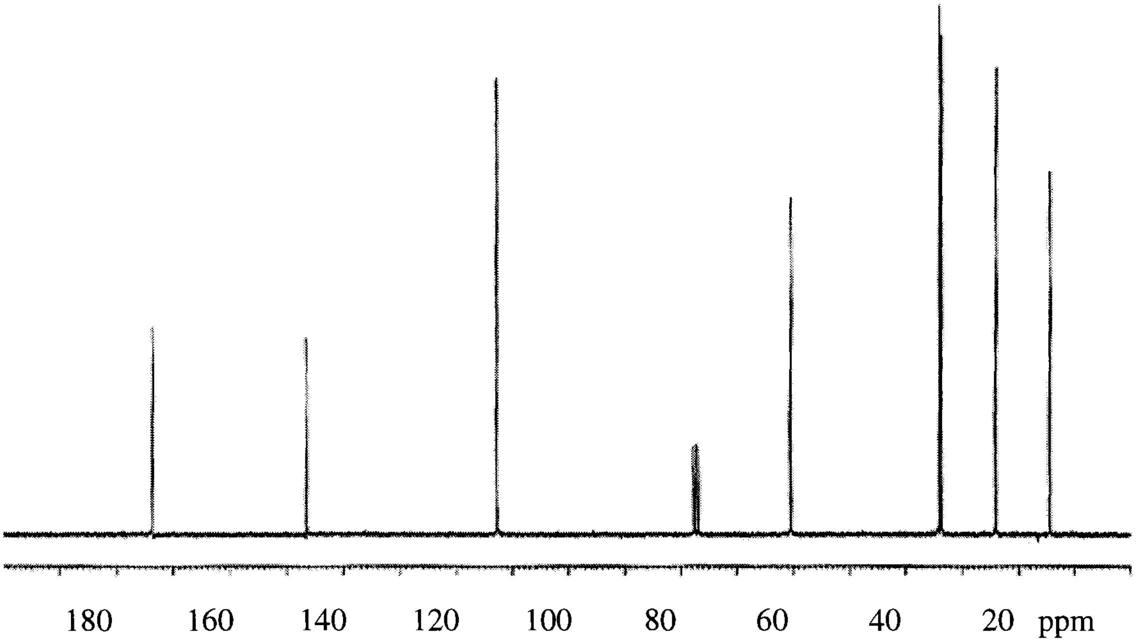
N9

Ethyl δ-iodobutyrate (^{13}C, $CDCl_3$)



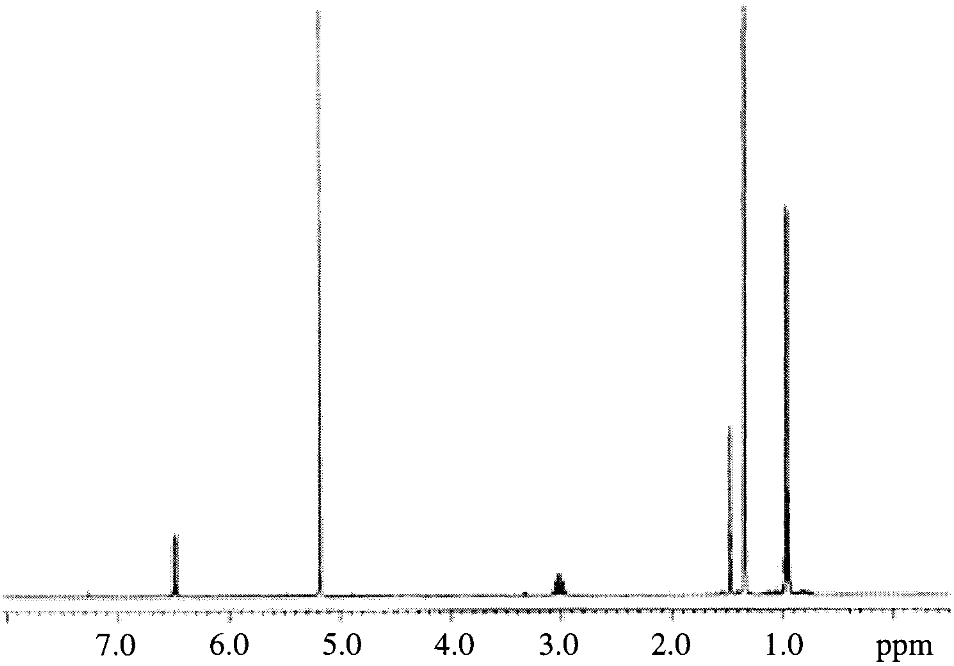
N10

2,3-Bis(4-ethoxy-4-oxo-butyl)-1,3-butadiene ($CDCl_3$)



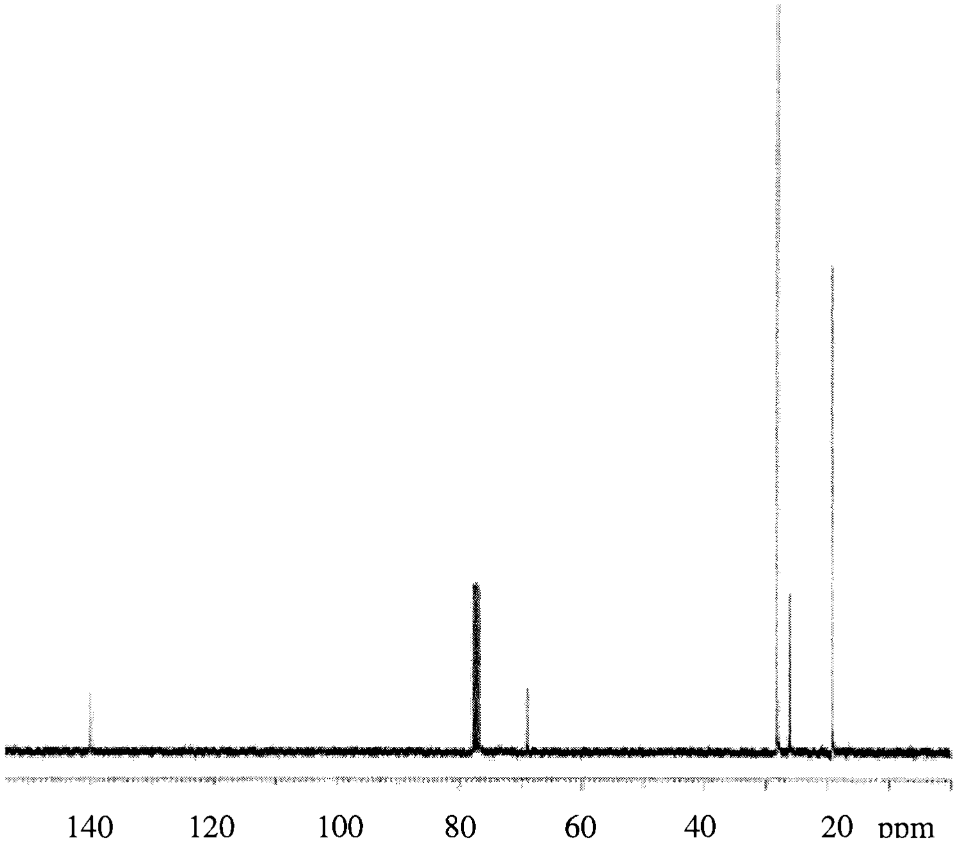
N11

2,3-Bis(4-ethoxy-4-oxo-butyl)-1,3-butadiene (^{13}C, $CDCl_3$)



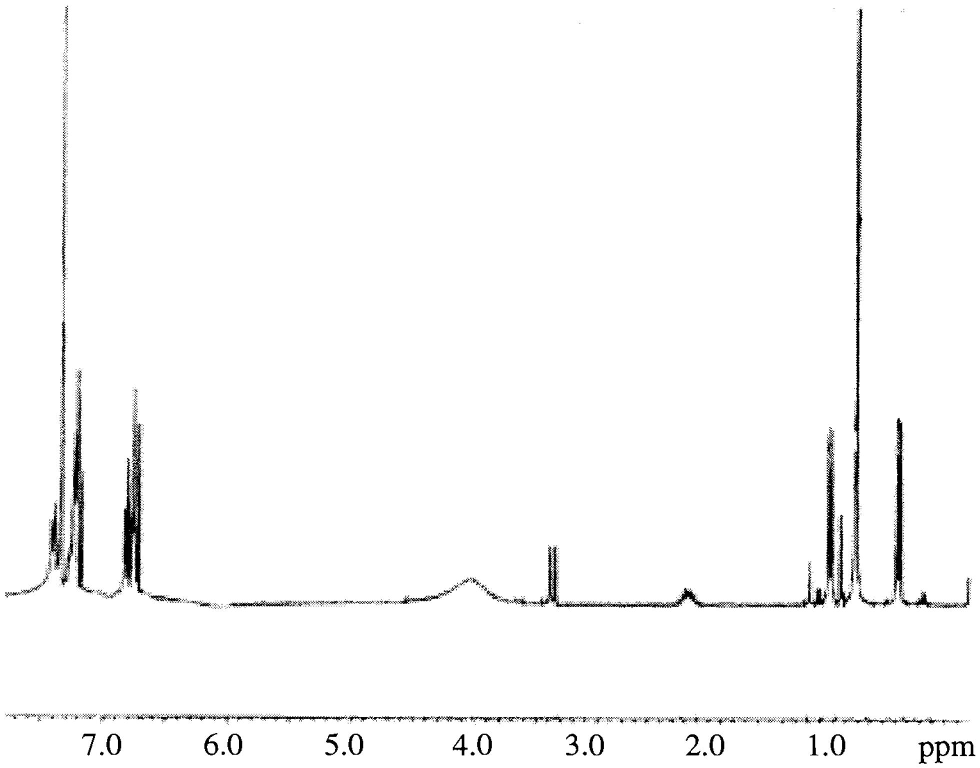
N12

***N-tert*-Butyl-α-*iso*-propylnitrone ($CDCl_3$)**



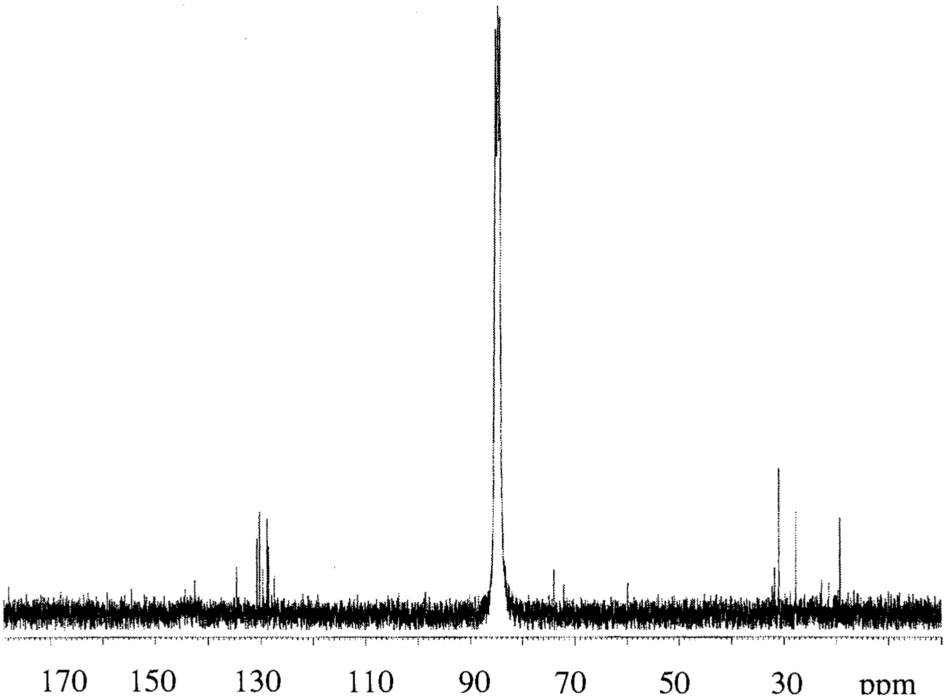
N13

***N-tert*-Butyl-α-*iso*-propylnitrone (^{13}C, $CDCl_3$)**



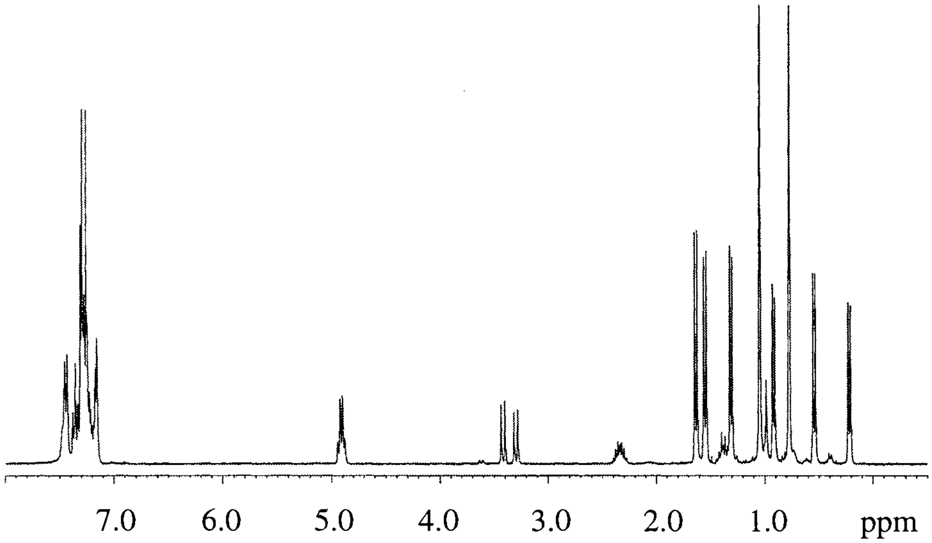
N14

2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide ($CDCl_3$)



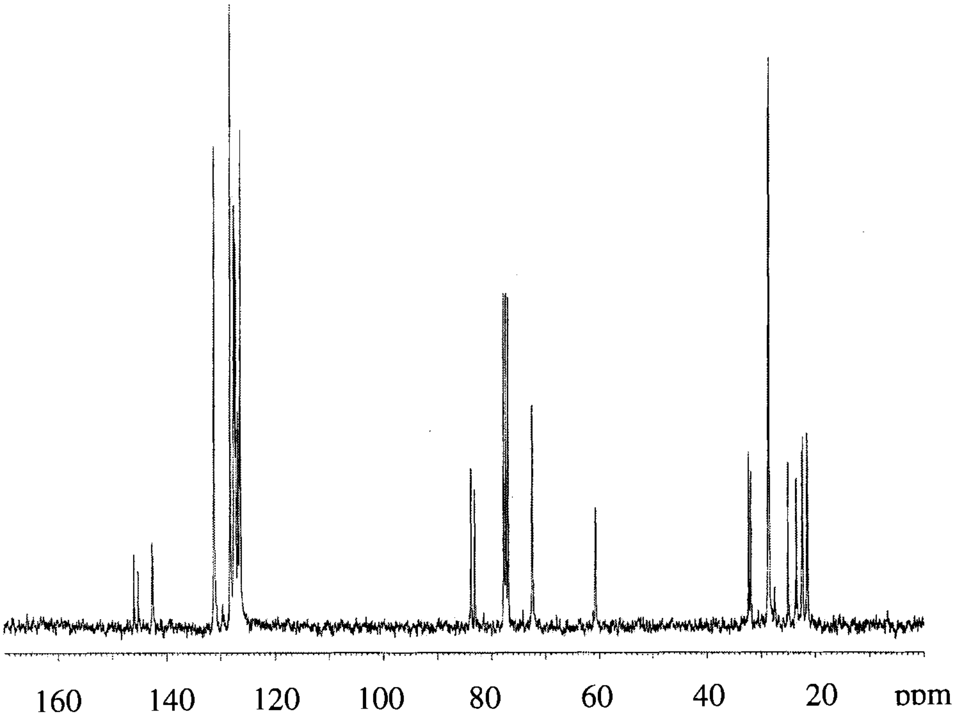
N15

2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide (^{13}C , $CDCl_3$)



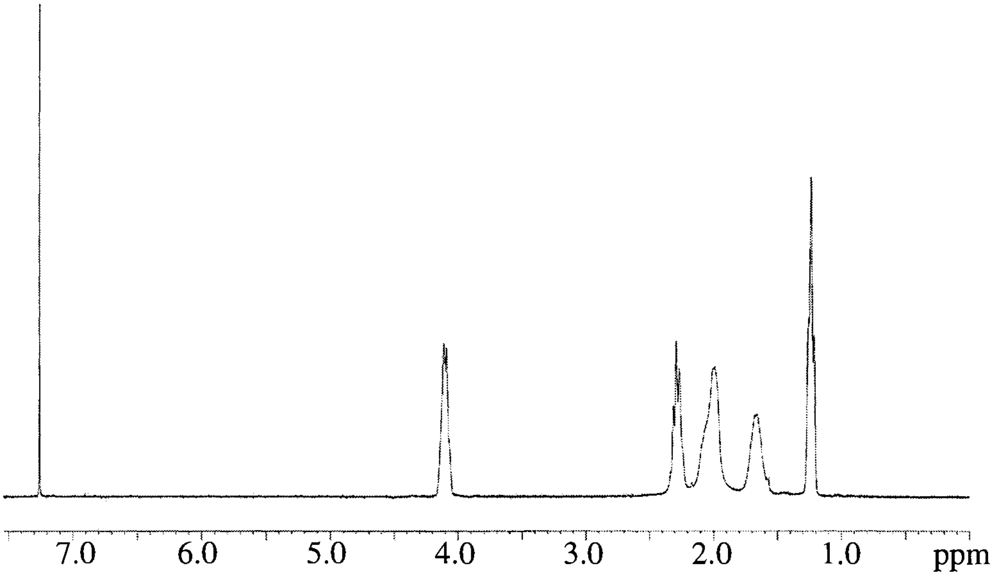
N16

2,2,5-Trimethyl-4-phenyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane ($CDCl_3$)



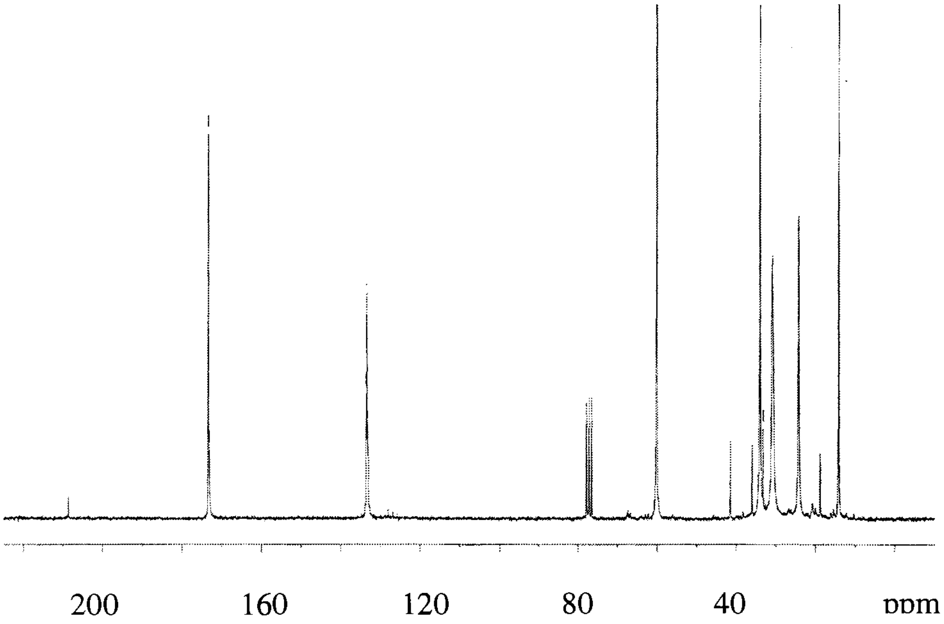
N17

2,2,5-Trimethyl-4-phenyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (^{13}C, $CDCl_3$)



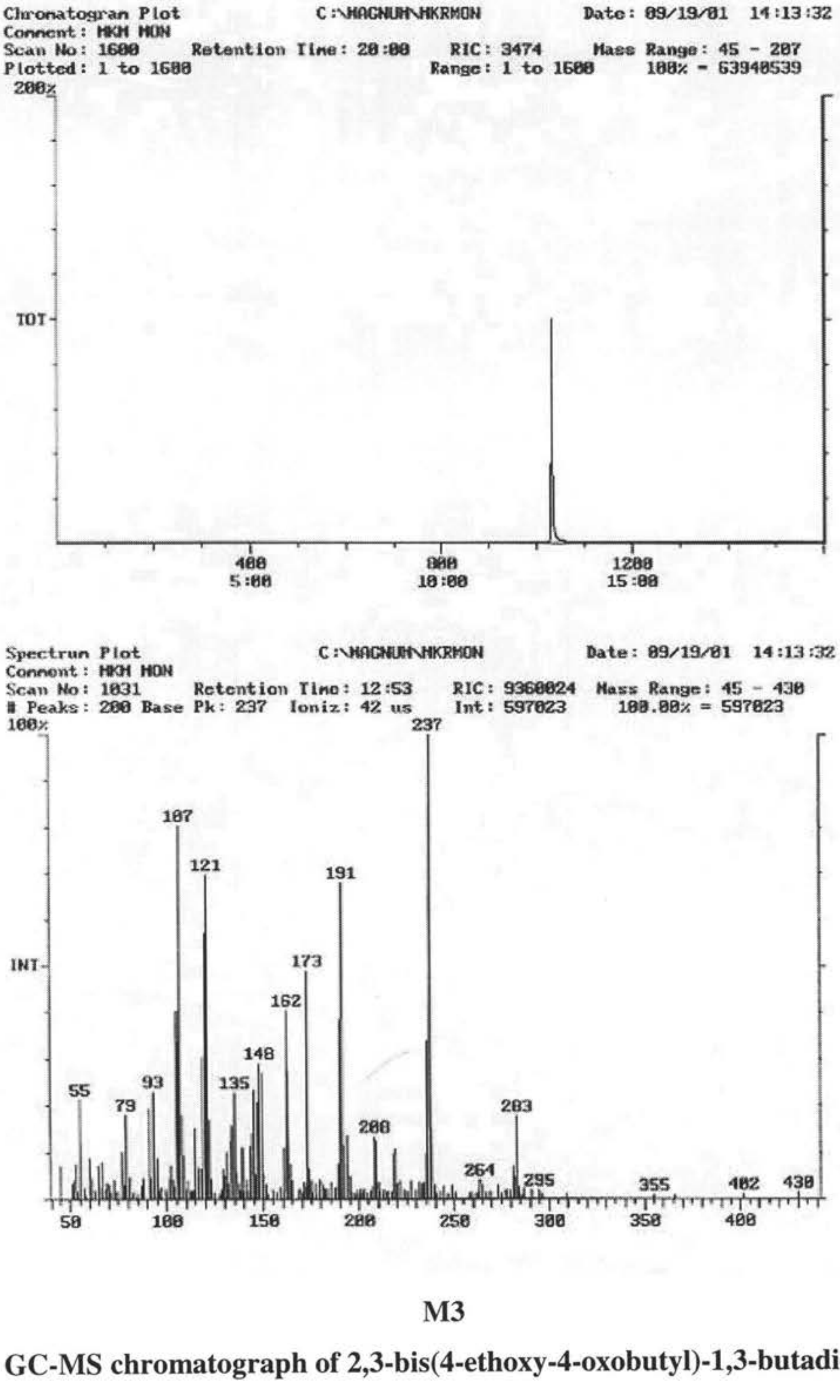
N18

Poly[2,3-Bis(4-ethoxy-4-oxo-butyl)-1,3-butadiene] ($CDCl_3$)



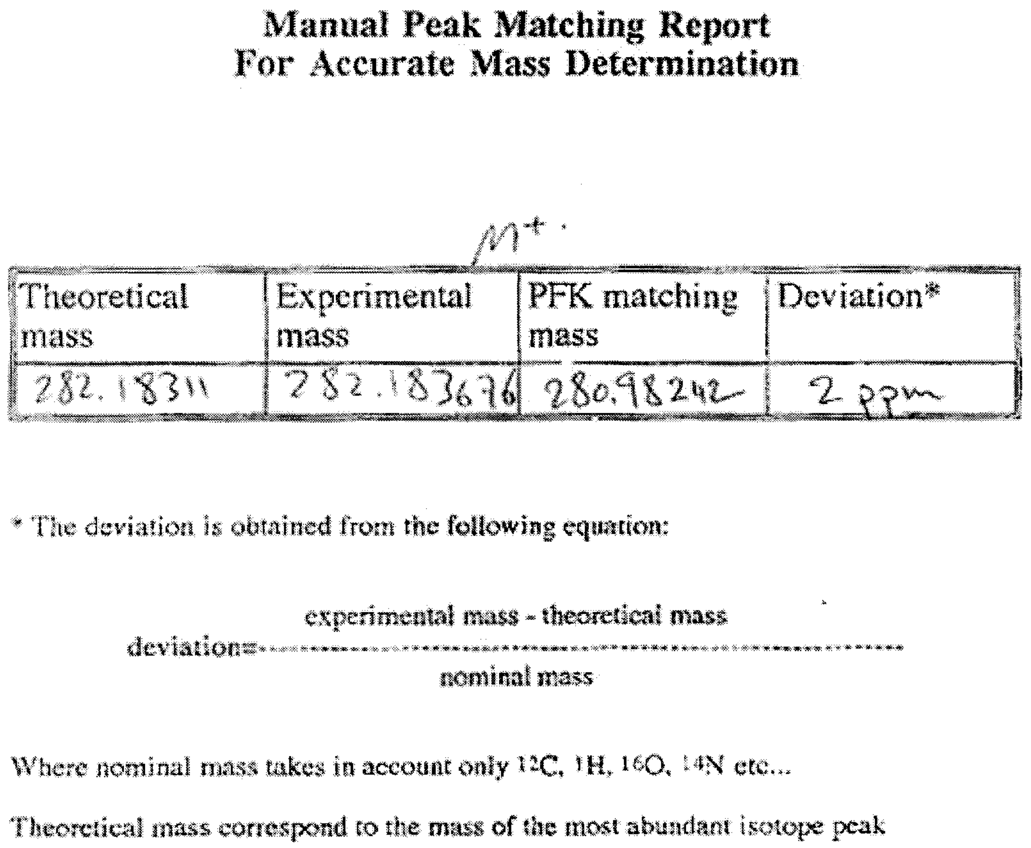
N19

Poly[2,3-Bis(4-ethoxy-4-oxo-butyl)-1,3-butadiene] (^{13}C, $CDCl_3$)



M3

GC-MS chromatograph of 2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene



Manual Peak Matching Report
For Accurate Mass Determination

$M^{+\cdot}$

Theoretical mass	Experimental mass	PFK matching mass	Deviation*
282.18311	282.183676	280.98242	2 ppm

* The deviation is obtained from the following equation:

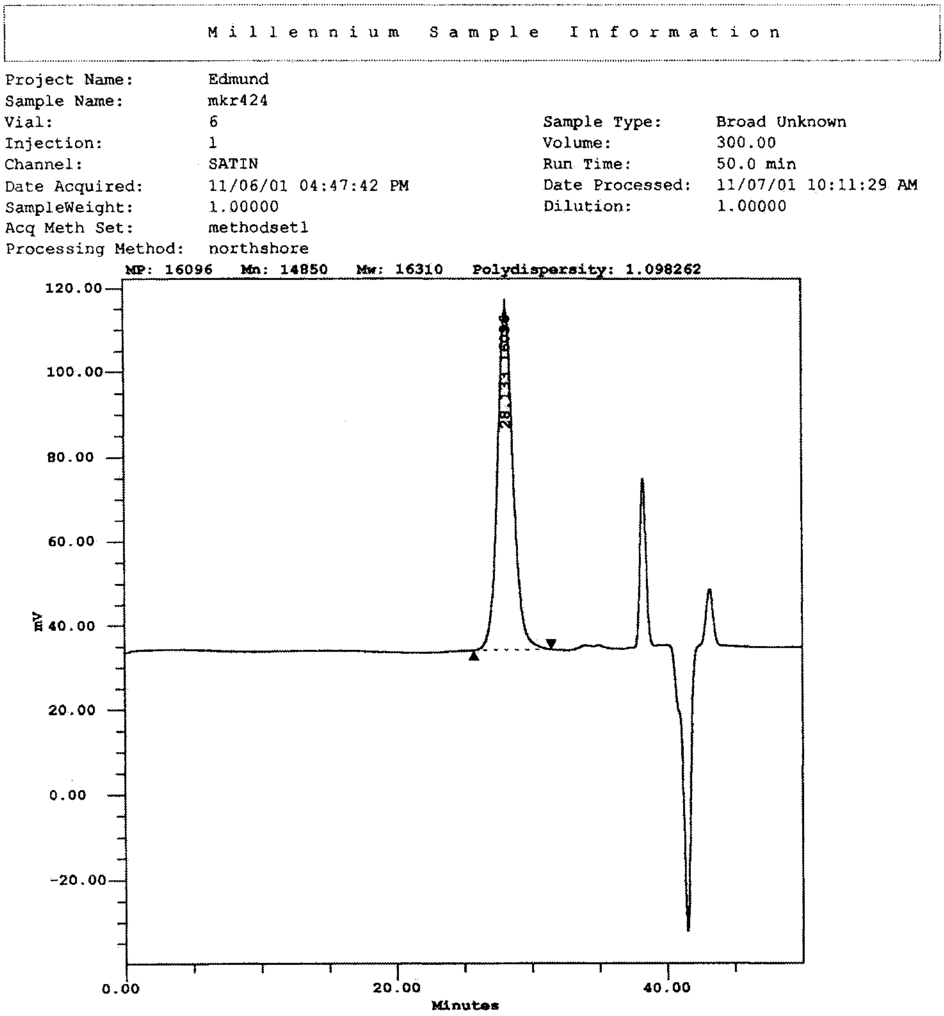
$$\text{deviation} = \frac{\text{experimental mass} - \text{theoretical mass}}{\text{nominal mass}}$$

Where nominal mass takes in account only ^{12}C, ^{1}H, ^{16}O, ^{14}N etc...

Theoretical mass correspond to the mass of the most abundant isotope peak

M4

High resolution mass spectrometry for 2,3-bis(-4-ethoxy-4-oxobutyl)-1,3-butadiene



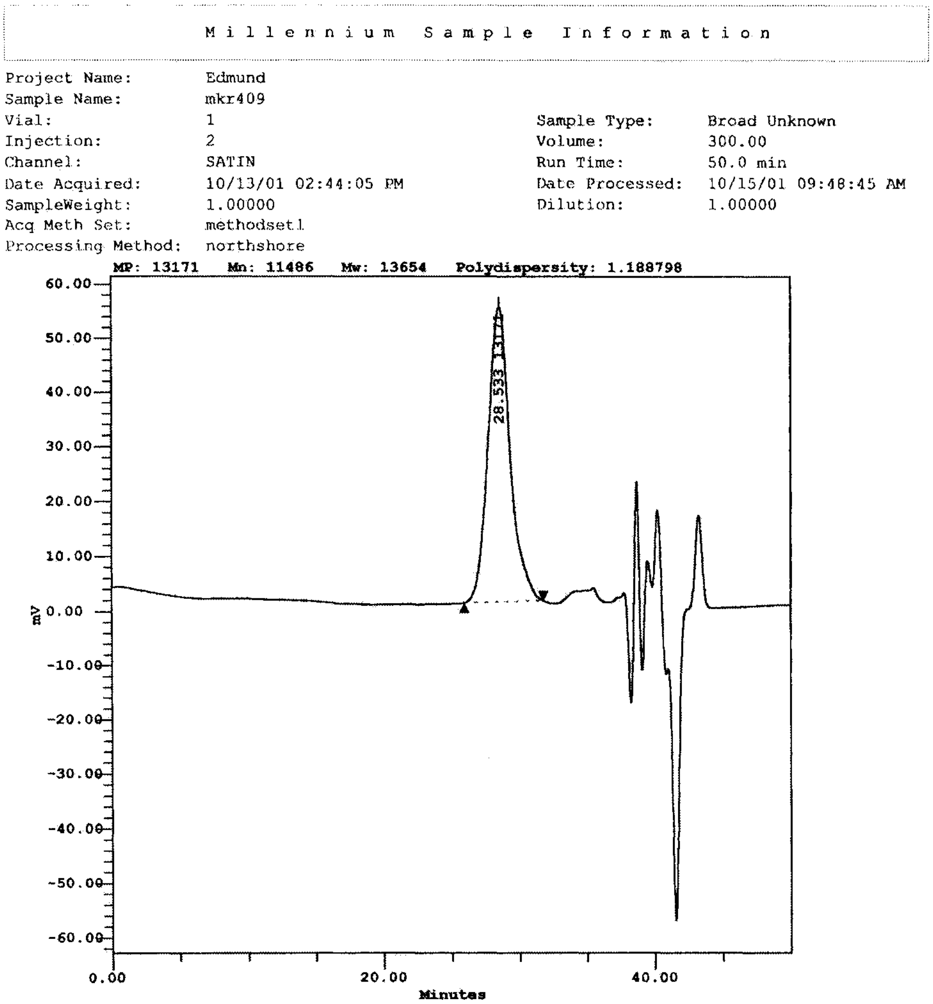
Millennium Sample Information

Project Name: Edmund
Sample Name: mkr424
Vial: 6
Injection: 1
Channel: SATIN
Date Acquired: 11/06/01 04:47:42 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 11/07/01 10:11:29 AM
Dilution: 1.00000

MP: 16096 Mn: 14850 Mw: 16310 Polydispersity: 1.098262

G15

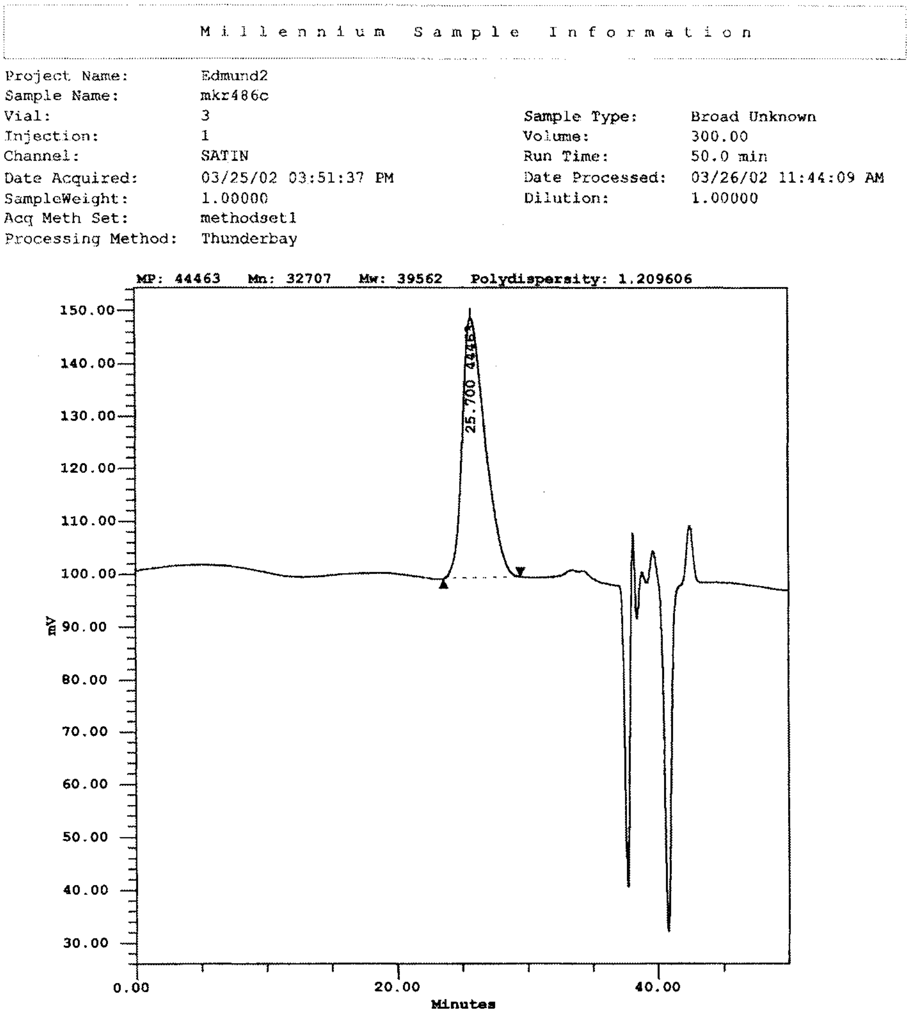


Millennium Sample Information

Project Name: Edmund
Sample Name: mkr409
Vial: 1
Injection: 2
Channel: SATIN
Date Acquired: 10/13/01 02:44:05 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 10/15/01 09:48:45 AM
Dilution: 1.00000

MP: 13171 Mn: 11486 Mw: 13654 Polydispersity: 1.188798

G16



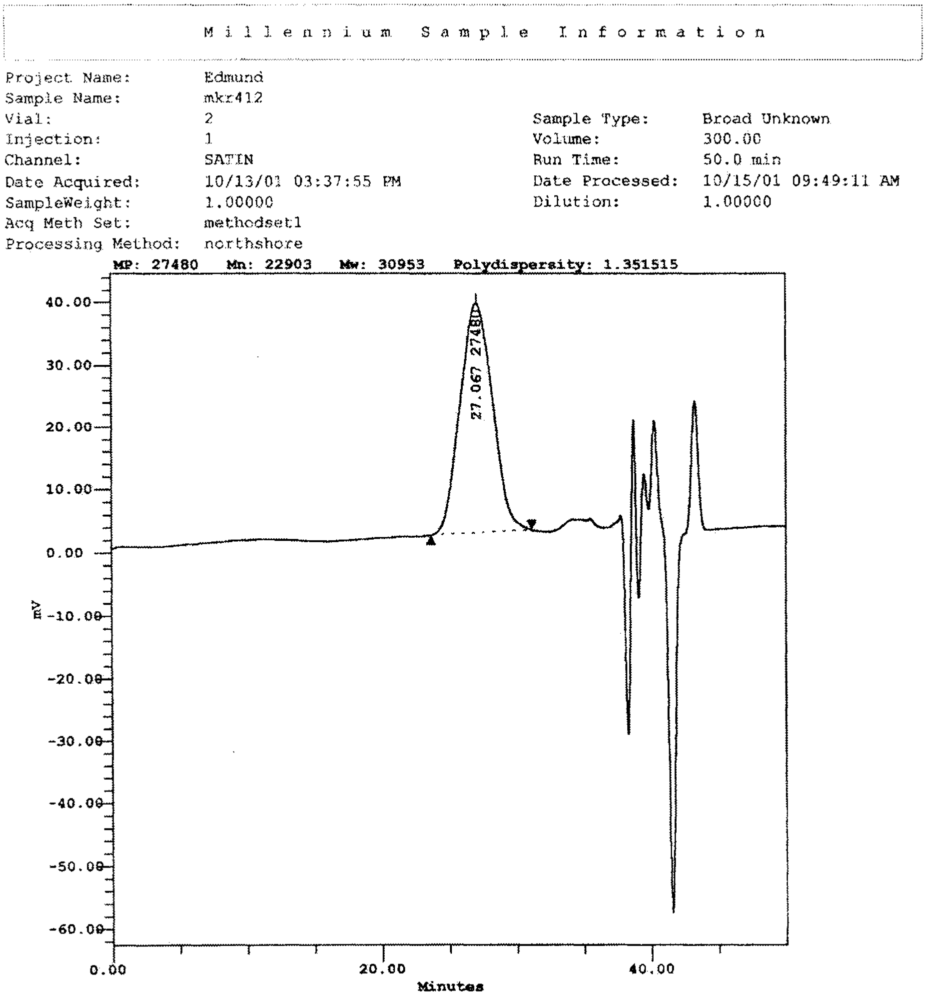
Millennium Sample Information

Project Name: Edmund2
Sample Name: mkr486c
Vial: 3
Injection: 1
Channel: SATIN
Date Acquired: 03/25/02 03:51:37 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: Thunderbay

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 03/26/02 11:44:09 AM
Dilution: 1.00000

MP: 44463 Mn: 32707 Mw: 39562 Polydispersity: 1.209606

G17



Millennium Sample Information

Project Name:	Edmund		
Sample Name:	mkr412		
Vial:	2	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	10/13/01 03:37:55 PM	Date Processed:	10/15/01 09:49:11 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		

MP: 27480 Mn: 22903 Mw: 30953 Polydispersity: 1.351515

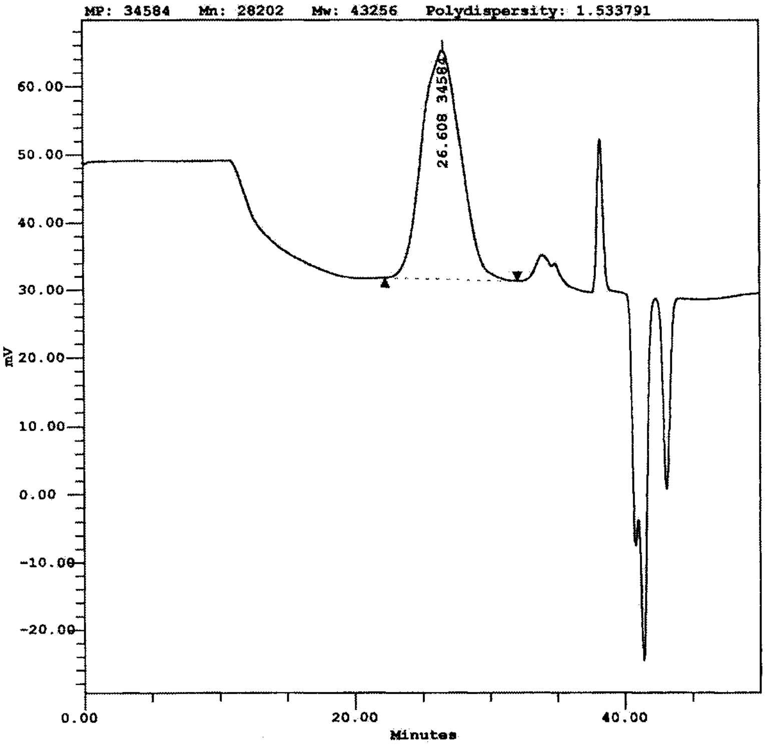
G18

Millennium Sample Information

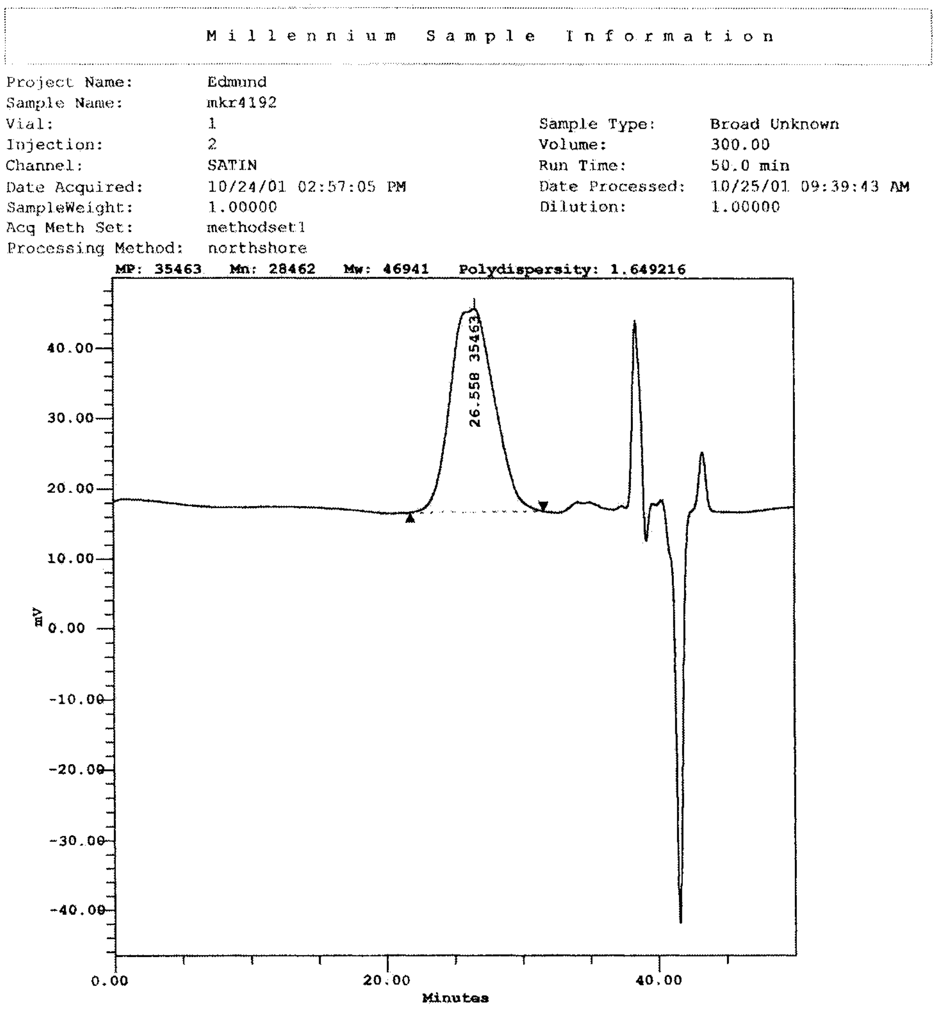
Project Name: Edmund
Sample Name: mkr426
Vial: 1
Injection: 2
Channel: SATIN
Date Acquired: 11/13/01 03:11:19 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 11/14/01 09:00:32 AM
Dilution: 1.00000

MP: 34584 Mn: 28202 Mw: 43256 Polydispersity: 1.533791



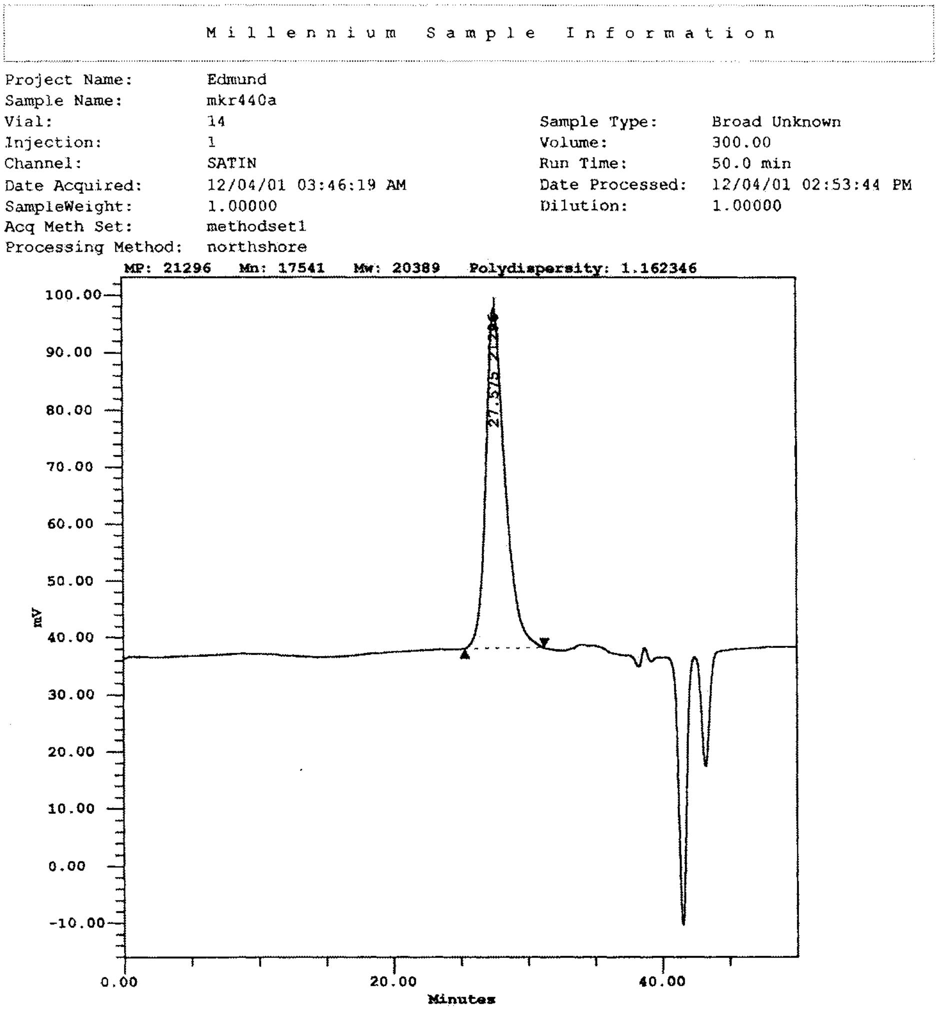
G19



```
                    Millennium Sample Information

Project Name:        Edmund
Sample Name:         mkr4192
Vial:                1                   Sample Type:       Broad Unknown
Injection:           2                   Volume:            300.00
Channel:             SATIN               Run Time:          50.0 min
Date Acquired:       10/24/01 02:57:05 PM Date Processed:   10/25/01 09:39:43 AM
SampleWeight:        1.00000             Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
     MP: 35463   Mn: 28462   Mw: 46941   Polydispersity: 1.649216
```

G20

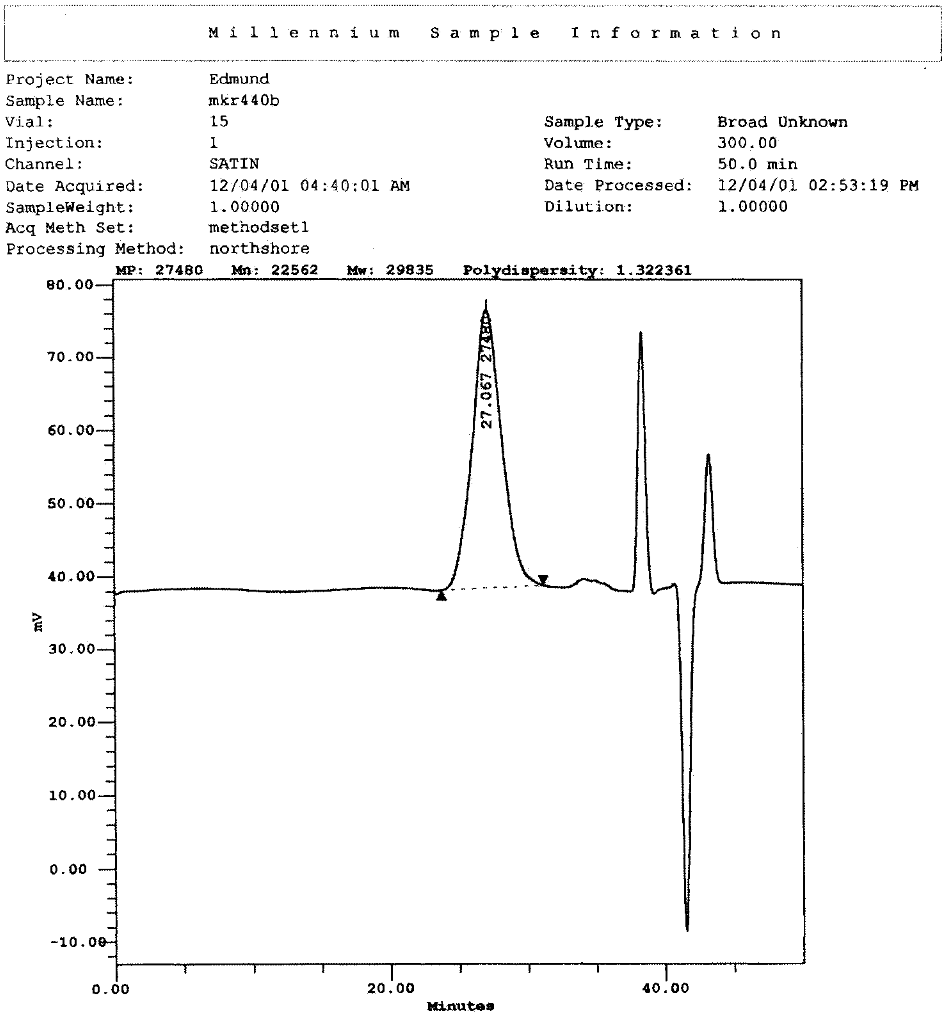


```
                    M i l l e n n i u m   S a m p l e   I n f o r m a t i o n

Project Name:        Edmund
Sample Name:         mkr440a
Vial:                14                             Sample Type:       Broad Unknown
Injection:           1                              Volume:            300.00
Channel:             SATIN                          Run Time:          50.0 min
Date Acquired:       12/04/01 03:46:19 AM           Date Processed:    12/04/01 02:53:44 PM
SampleWeight:        1.00000                        Dilution:          1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
```

MP: 21296   Mn: 17541   Mw: 20389   Polydispersity: 1.162346

G21

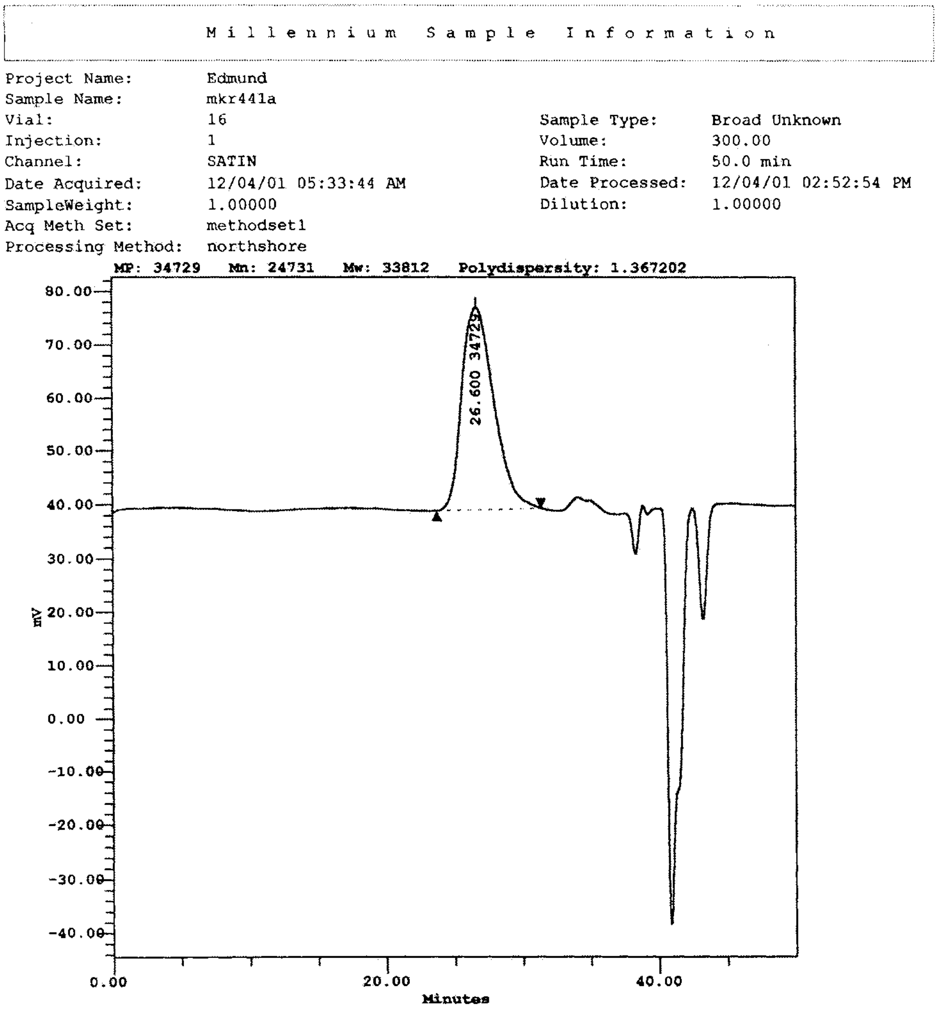


Millennium Sample Information

Project Name:	Edmund		
Sample Name:	mkr440b		
Vial:	15	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	12/04/01 04:40:01 AM	Date Processed:	12/04/01 02:53:19 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		

MP: 27480 Mn: 22562 Mw: 29835 Polydispersity: 1.322361

G22



Millennium Sample Information

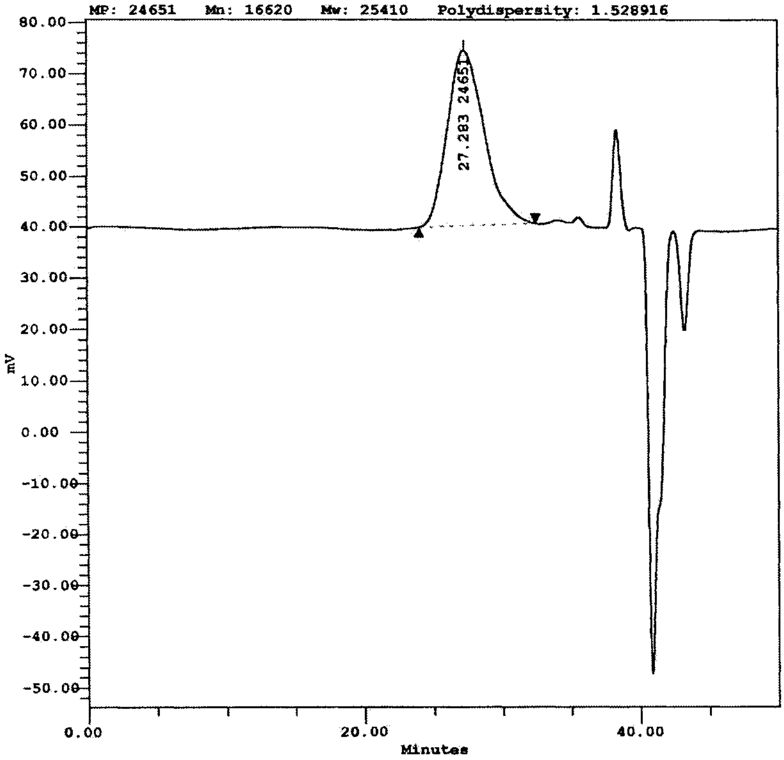
Project Name: Edmund
Sample Name: mkr441a
Vial: 16
Injection: 1
Channel: SATIN
Date Acquired: 12/04/01 05:33:44 AM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 12/04/01 02:52:54 PM
Dilution: 1.00000

MP: 34729 Mn: 24731 Mw: 33812 Polydispersity: 1.367202

G23

```
                    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:        Edmund
Sample Name:         mkr441b
Vial:                17                              Sample Type:      Broad Unknown
Injection:           1                               Volume:           300.00
Channel:             SATIN                           Run Time:         50.0 min
Date Acquired:       12/04/01 06:27:28 AM            Date Processed:   12/04/01 02:52:28 PM
SampleWeight:        1.00000                         Dilution:         1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
```

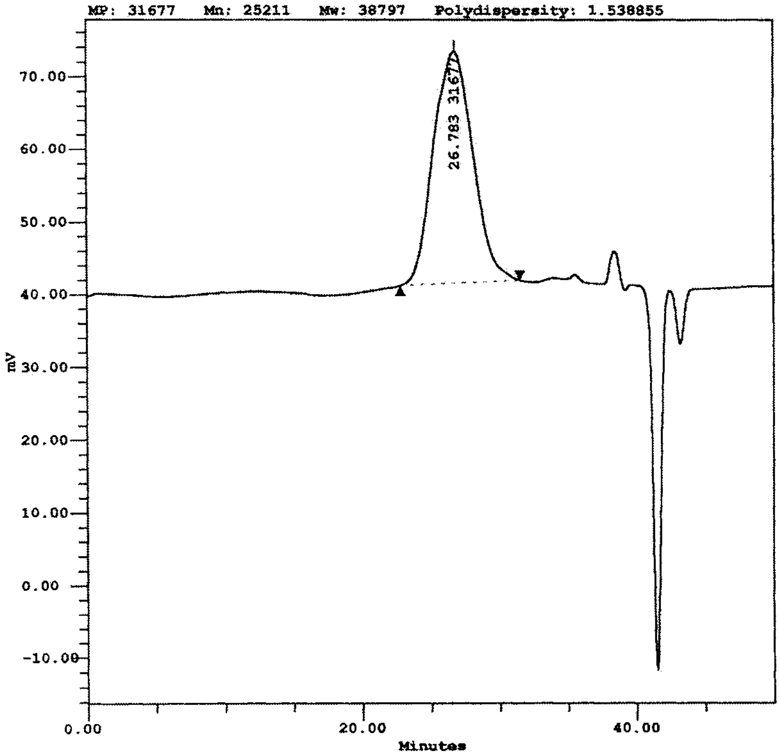


G24

Millennium Sample Information

Project Name: Edmund
Sample Name: mkr442a
Vial: 18
Injection: 1
Channel: SATIN
Date Acquired: 12/04/01 07:21:12 AM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 12/04/01 02:51:13 PM
Dilution: 1.00000

MP: 31677 Mn: 25211 Mw: 38797 Polydispersity: 1.538855

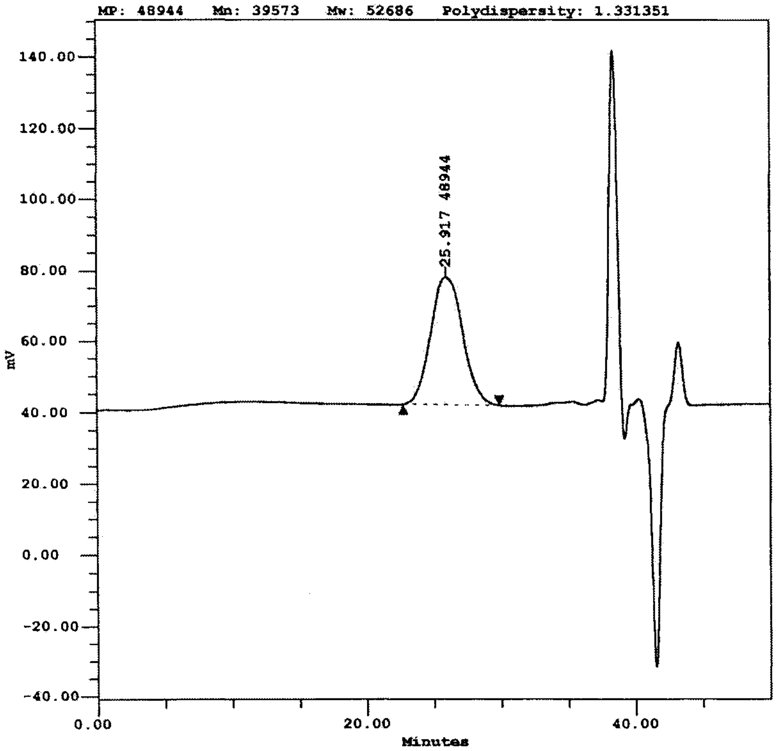


G25

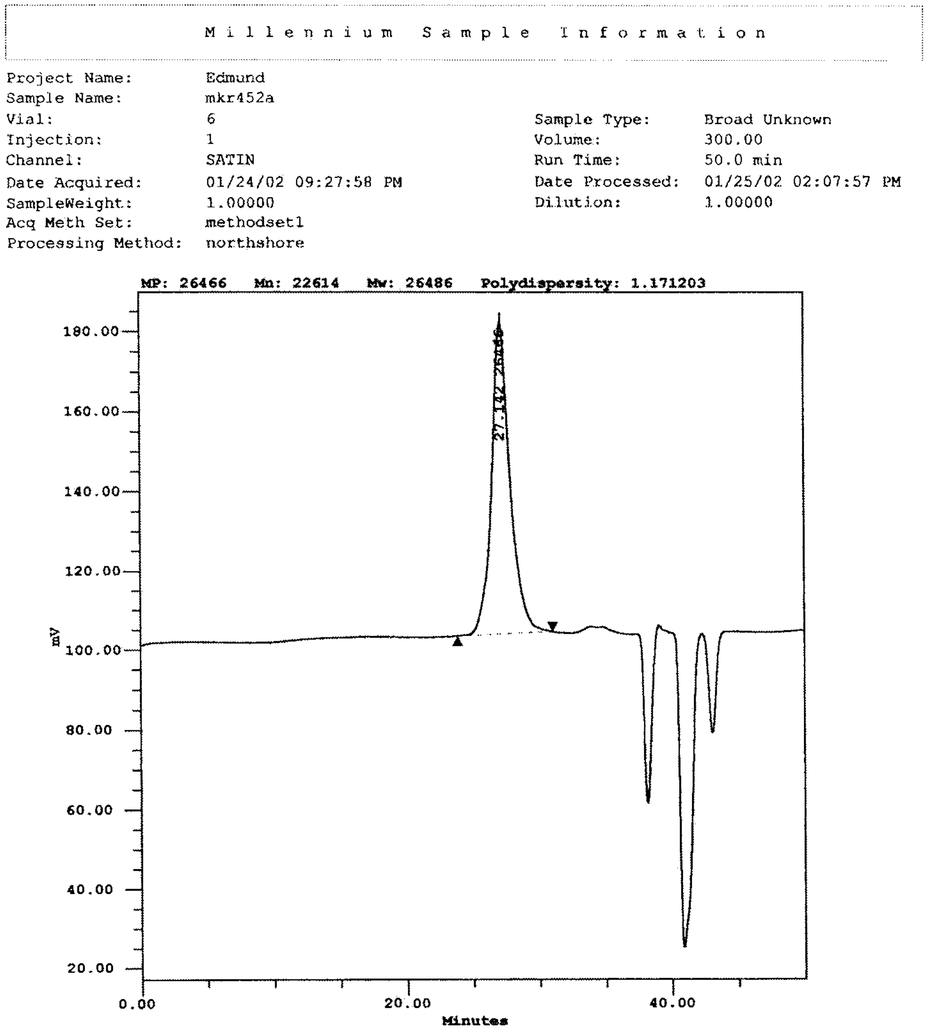
Millennium Sample Information

Project Name: Edmund
Sample Name: mkr442b
Vial: 19
Injection: 1
Channel: SATIN
Date Acquired: 12/04/01 08:14:56 AM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 12/04/01 02:50:47 PM
Dilution: 1.00000



G26



Millennium Sample Information

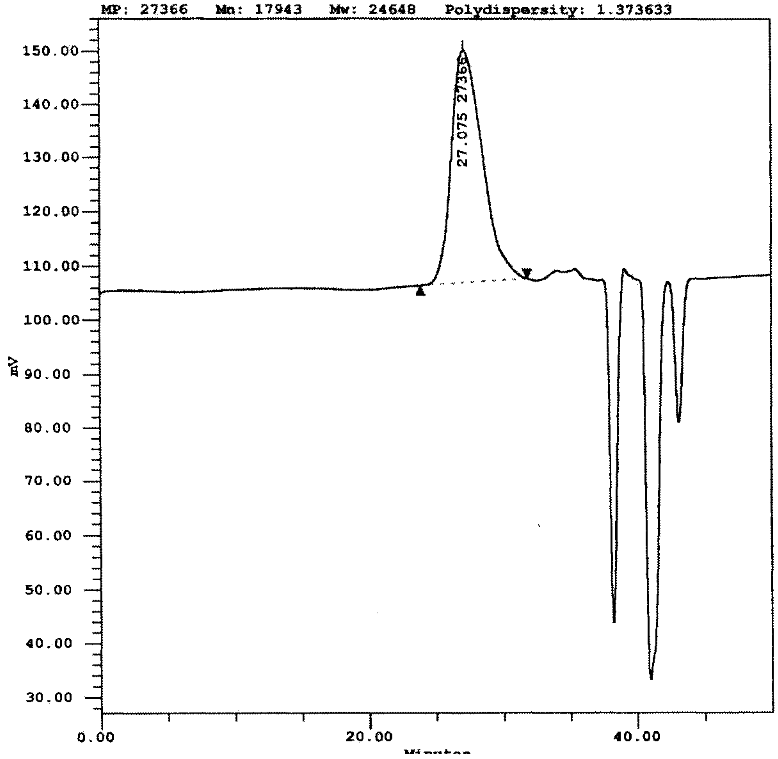
Project Name: Edmund
Sample Name: mkr452a
Vial: 6
Injection: 1
Channel: SATIN
Date Acquired: 01/24/02 09:27:58 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 01/25/02 02:07:57 PM
Dilution: 1.00000

MP: 26466 Mn: 22614 Mw: 26486 Polydispersity: 1.171203

G27

```
                    Millennium Sample Information

Project Name:       Edmund
Sample Name:        mkr452b
Vial:               7                           Sample Type:     Broad Unknown
Injection:          1                           Volume:          300.00
Channel:            SATIN                       Run Time:        50.0 min
Date Acquired:      01/24/02 10:21:42 PM        Date Processed:  01/25/02 02:08:24 PM
SampleWeight:       1.00000                     Dilution:        1.00000
Acq Meth Set:       methodset1
Processing Method:  northshore
```

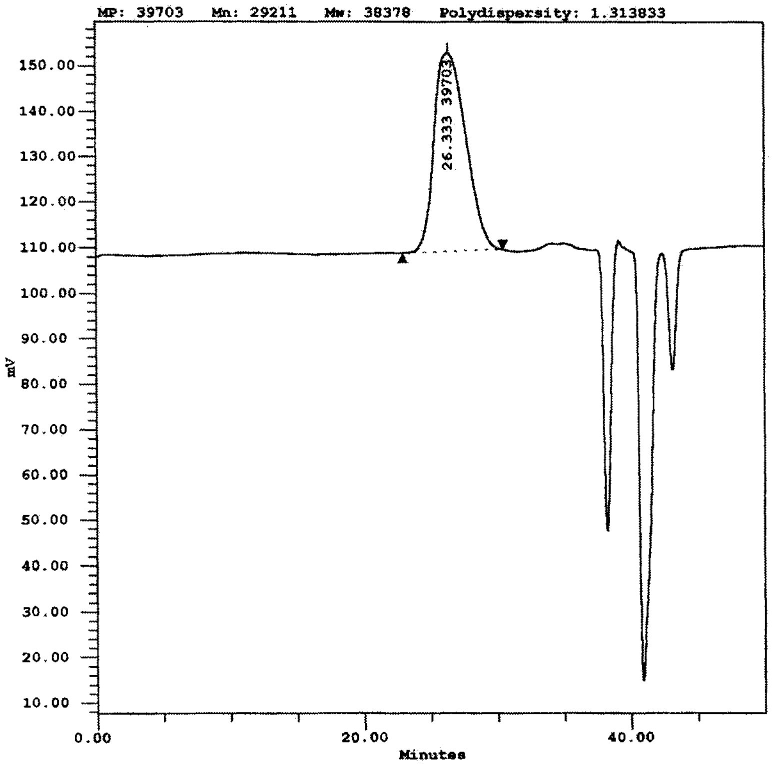


G28

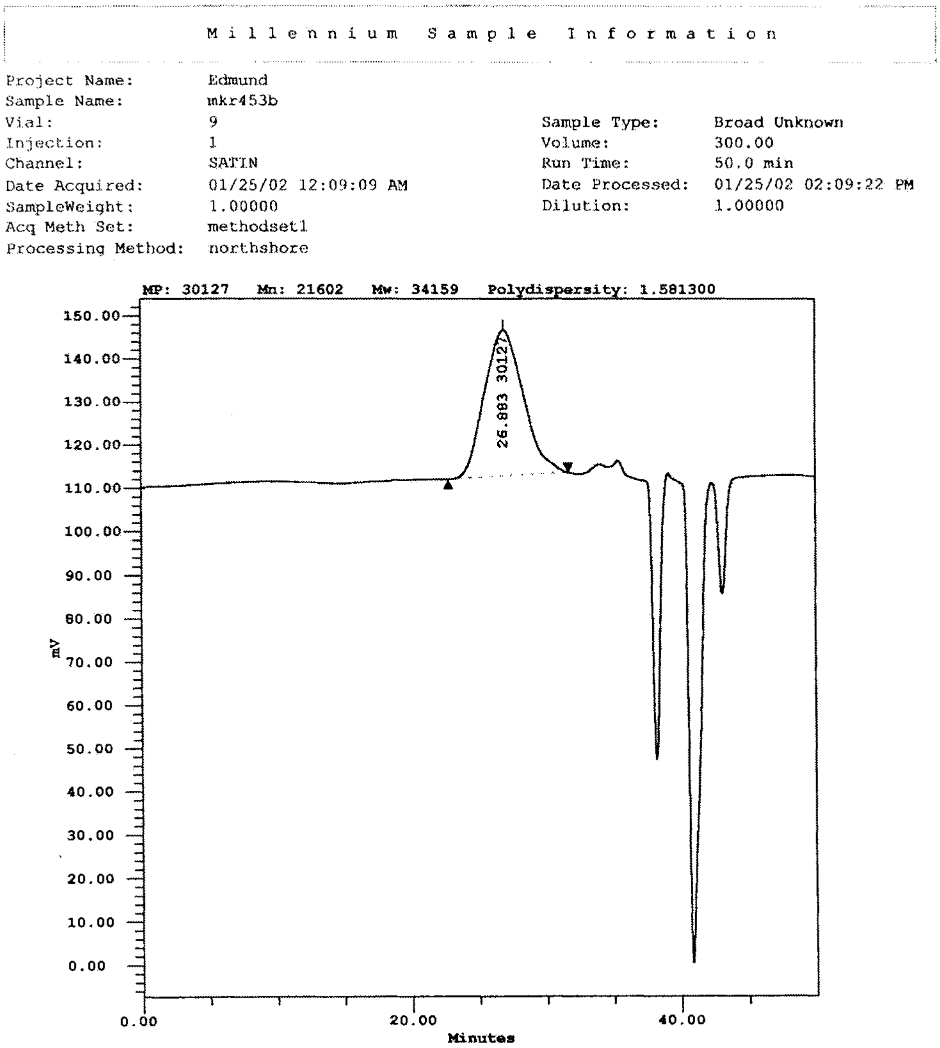
Millennium Sample Information

Project Name: Edmund
Sample Name: mkr453a
Vial: 8
Injection: 1
Channel: SATIN
Date Acquired: 01/24/02 11:15:25 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 01/25/02 02:08:59 PM
Dilution: 1.00000



G29



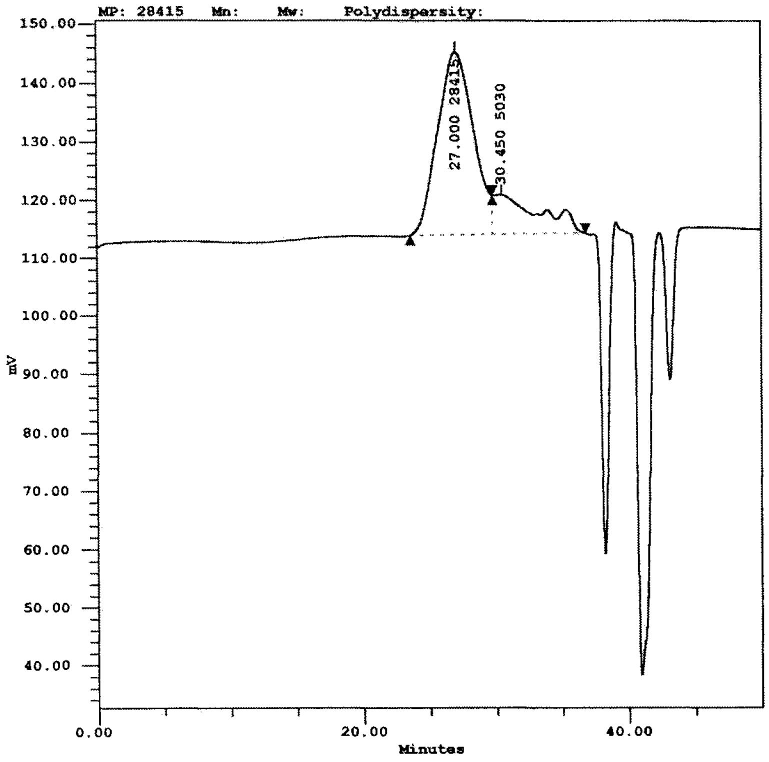
```
                     Millennium Sample Information

Project Name:        Edmund
Sample Name:         mkr453b
Vial:                9                         Sample Type:      Broad Unknown
Injection:           1                         Volume:           300.00
Channel:             SATIN                     Run Time:         50.0 min
Date Acquired:       01/25/02 12:09:09 AM      Date Processed:   01/25/02 02:09:22 PM
SampleWeight:        1.00000                   Dilution:         1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
```

G30

```
                     Millennium Sample Information

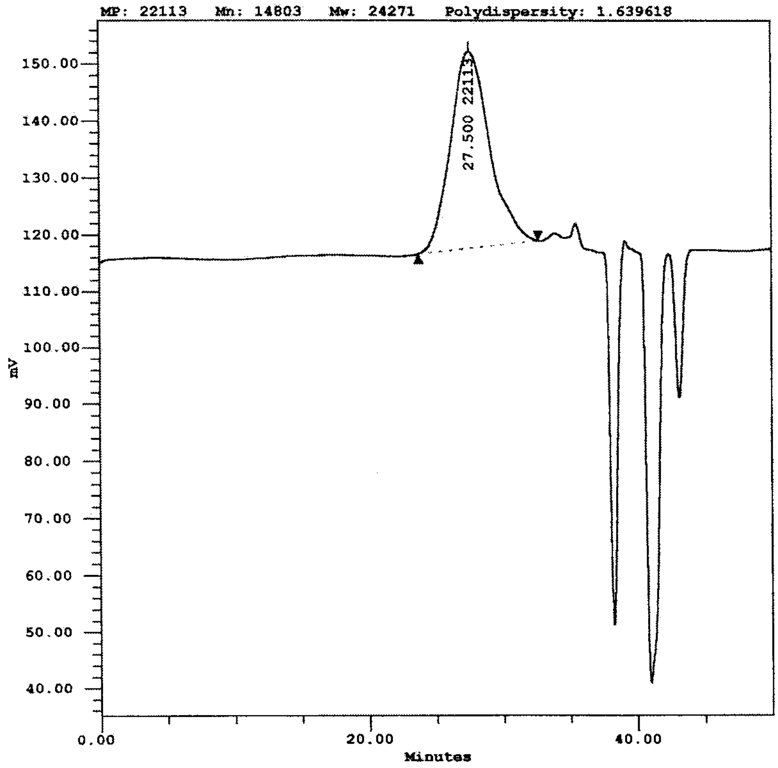
Project Name:       Edmund
Sample Name:        mkr454a2
Vial:               10                         Sample Type:      Broad Unknown
Injection:          1                          Volume:           300.00
Channel:            SATIN                      Run Time:         50.0 min
Date Acquired:      01/25/02 01:02:51 AM       Date Processed:   01/25/02 02:09:57 PM
SampleWeight:       1.00000                    Dilution:         1.00000
Acq Meth Set:       methodset1
Processing Method:  northshore
```



G31

Millennium Sample Information

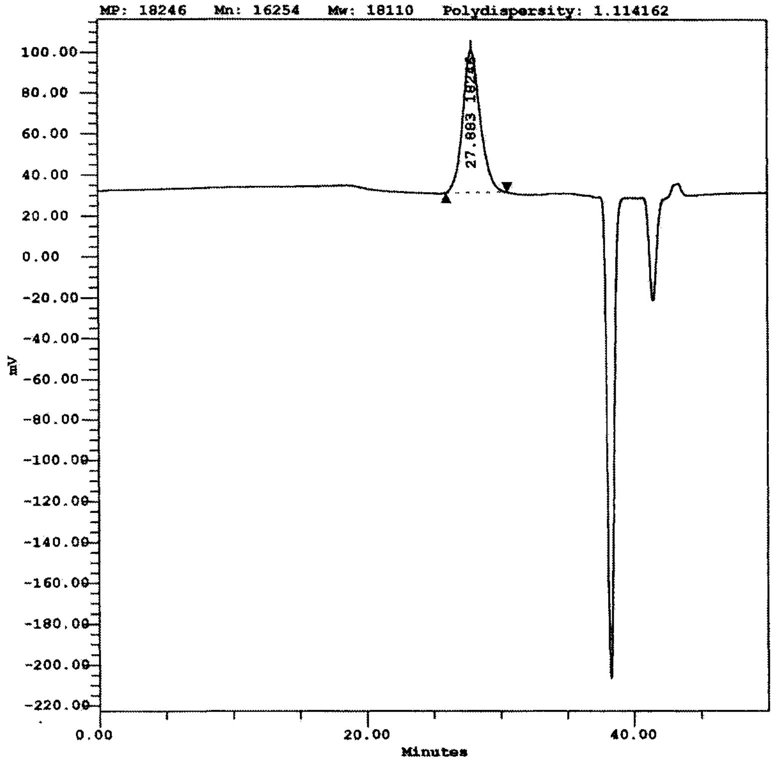
Project Name:	Edmund		
Sample Name:	mkr454b		
Vial:	11	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	01/25/02 01:56:37 AM	Date Processed:	01/25/02 02:10:46 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		



G32

```
                    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:        Edmund
Sample Name:         mkr462A
Vial:                2                          Sample Type:      Broad Unknown
Injection:           1                          Volume:           300.00
Channel:             SATIN                      Run Time:         50.0 min
Date Acquired:       02/06/02 12:23:23 PM       Date Processed:   02/07/02 11:36:40 AM
SampleWeight:        1.00000                    Dilution:         1.00000
Acq Meth Set:        methodset1
Processing Method:   northshore
```

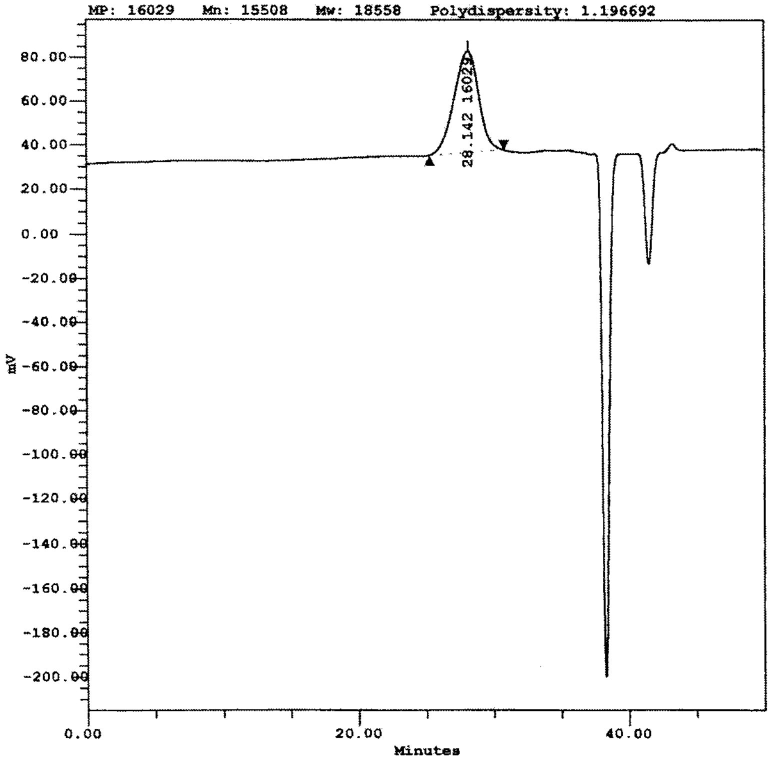


G33

```
                    Millennium Sample Information

Project Name:       Edmund
Sample Name:        mkr462B
Vial:               3                       Sample Type:      Broad Unknown
Injection:          1                       Volume:           300.00
Channel:            SATIN                   Run Time:         50.0 min
Date Acquired:      02/06/02 01:17:06 PM    Date Processed:   02/07/02 11:37:07 AM
SampleWeight:       1.00000                 Dilution:         1.00000
Acq Meth Set:       methodset1
Processing Method:  northshore
```

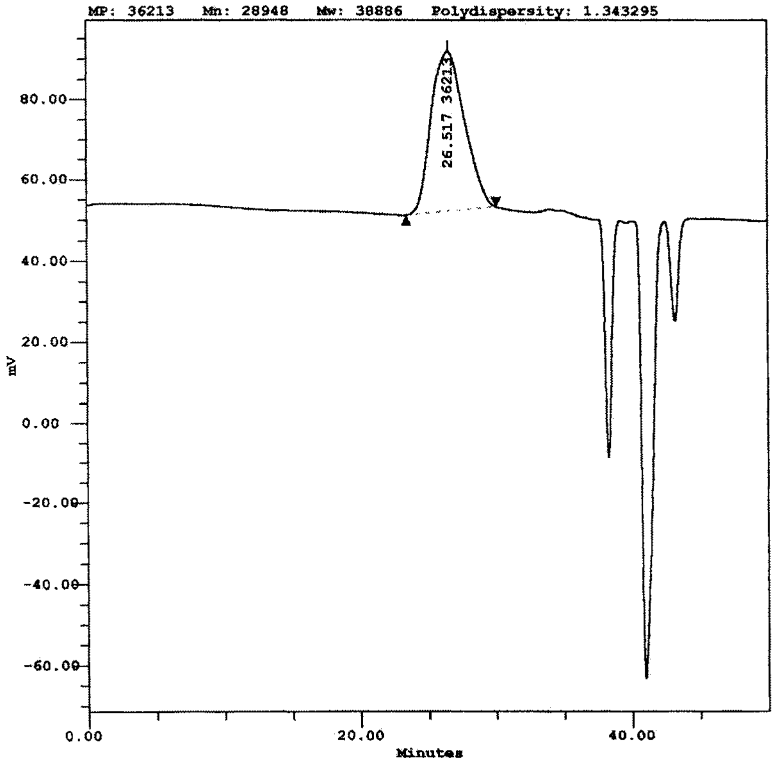
MP: 16029   Mn: 15508   Mw: 18558   Polydispersity: 1.196692



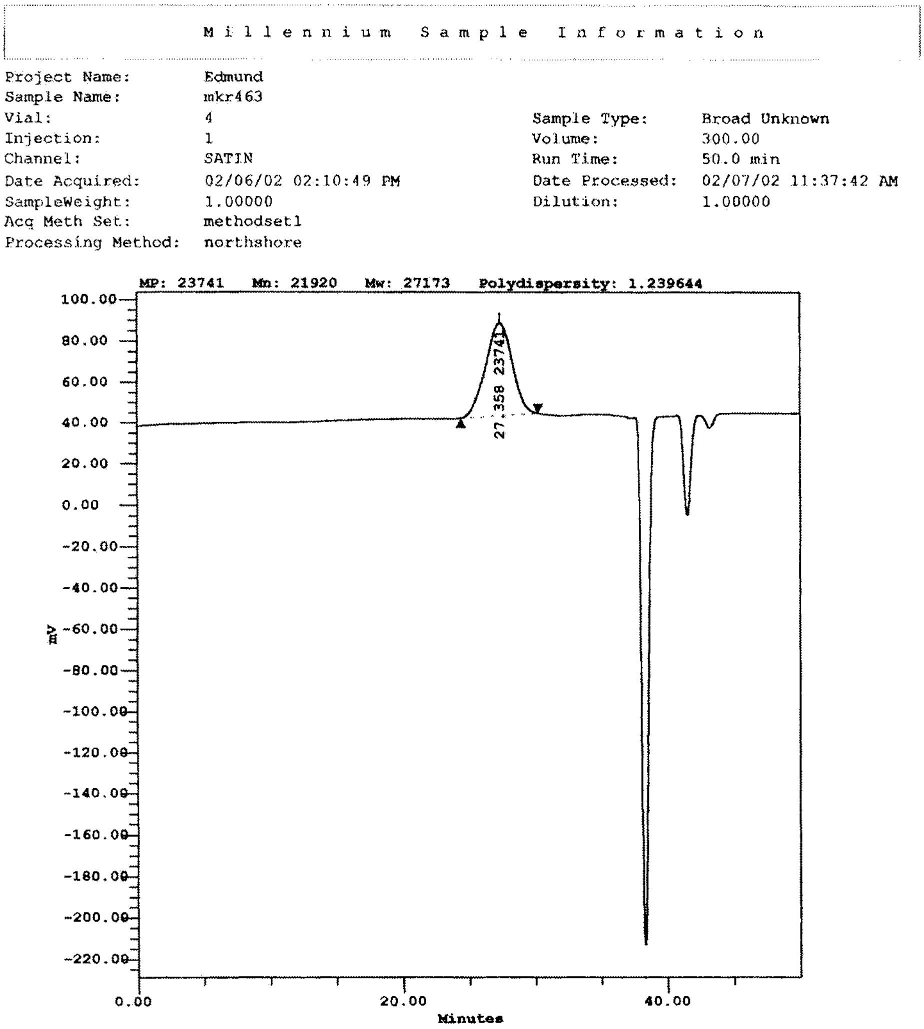
G34

Millennium Sample Information

Project Name:	Edmund		
Sample Name:	mkr461c		
Vial:	2	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	02/13/02 01:37:12 AM	Date Processed:	02/13/02 09:43:30 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		



G35



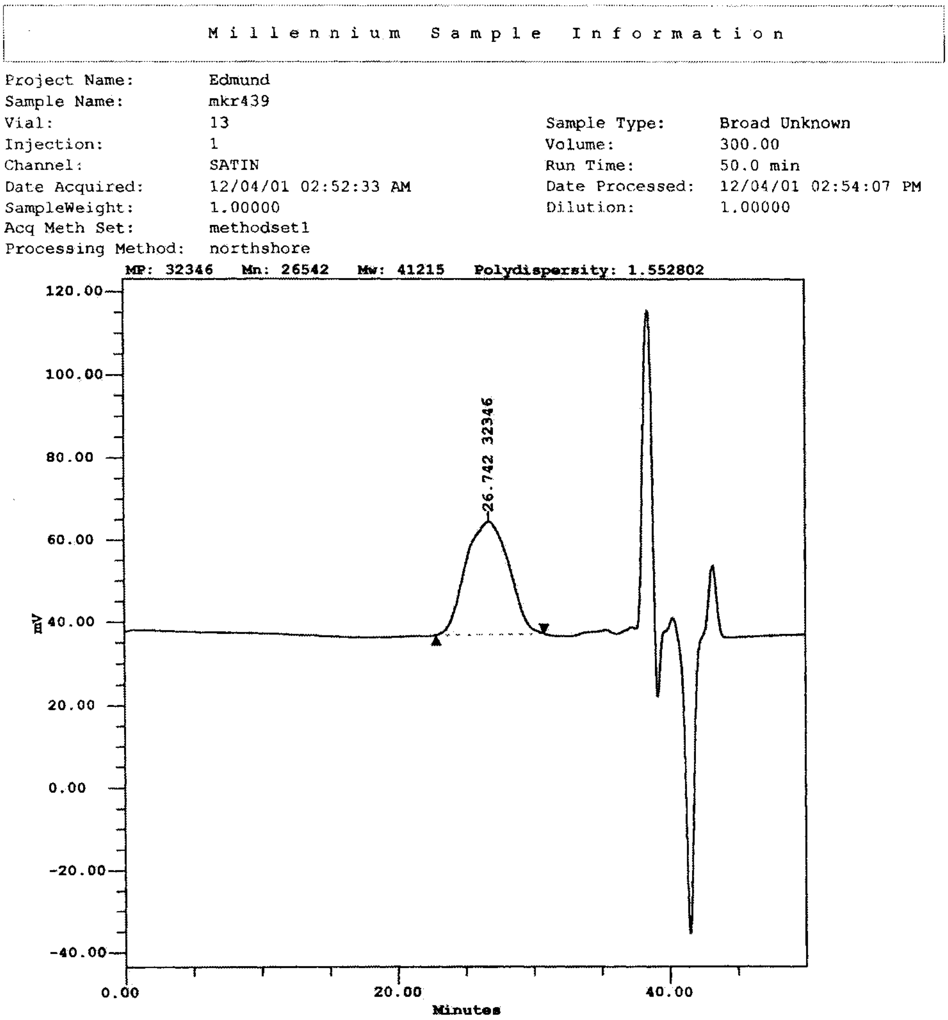
Millennium Sample Information

Project Name: Edmund
Sample Name: mkr463
Vial: 4
Injection: 1
Channel: SATIN
Date Acquired: 02/06/02 02:10:49 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 02/07/02 11:37:42 AM
Dilution: 1.00000

MP: 23741 Mn: 21920 Mw: 27173 Polydispersity: 1.239644

G36



Millennium Sample Information

Project Name: Edmund
Sample Name: mkr439
Vial: 13
Injection: 1
Channel: SATIN
Date Acquired: 12/04/01 02:52:33 AM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore

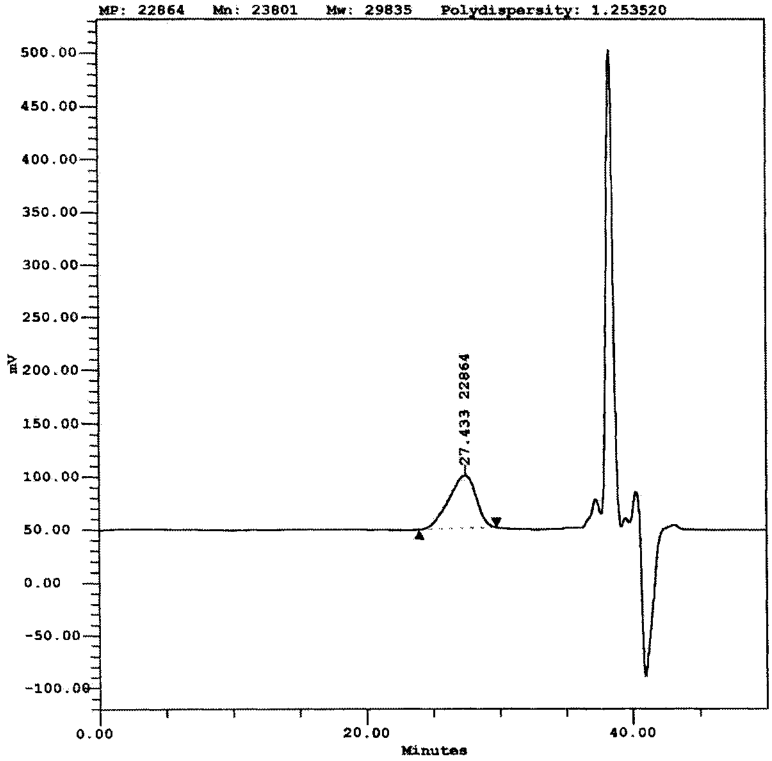
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 12/04/01 02:54:07 PM
Dilution: 1.00000

MP: 32346 Mn: 26542 Mw: 41215 Polydispersity: 1.552802

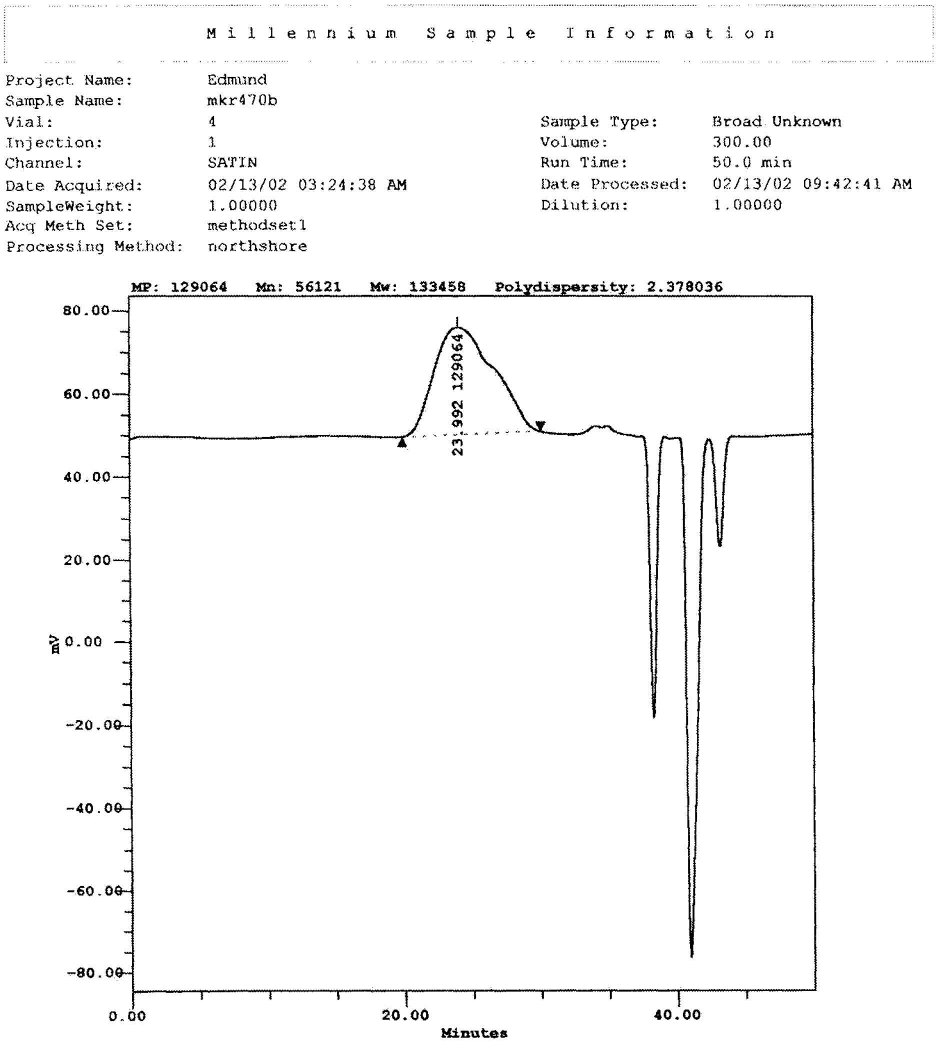
G37

Millennium Sample Information

Project Name:	Edmund		
Sample Name:	mkr470a		
Vial:	3	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	02/13/02 02:30:55 AM	Date Processed:	02/13/02 09:43:05 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		



G38



Millennium Sample Information

Project Name: Edmund
Sample Name: mkr470b
Vial: 4
Injection: 1
Channel: SATIN
Date Acquired: 02/13/02 03:24:38 AM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 02/13/02 09:42:41 AM
Dilution: 1.00000

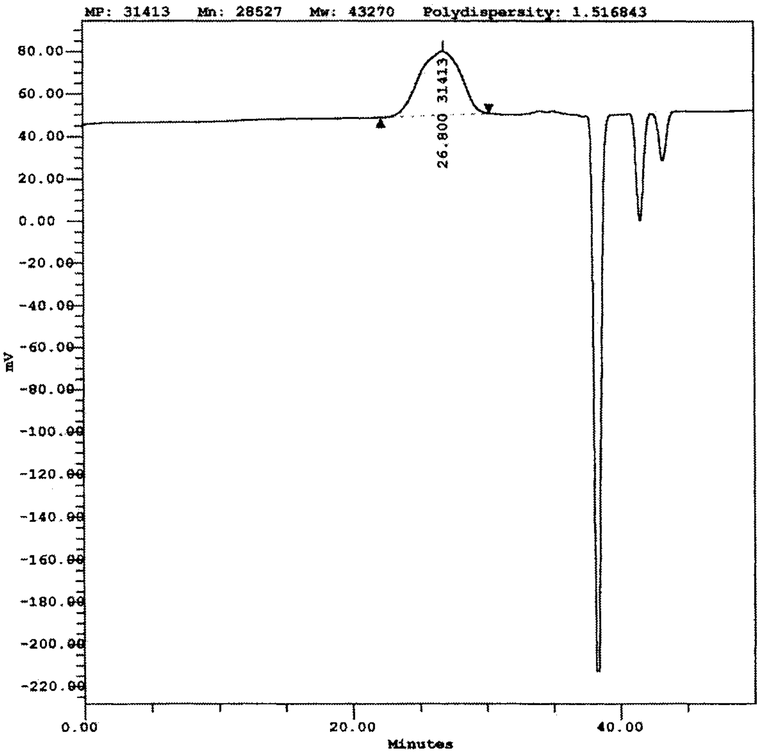
MP: 129064 Mn: 56121 Mw: 133458 Polydispersity: 2.378036

G39

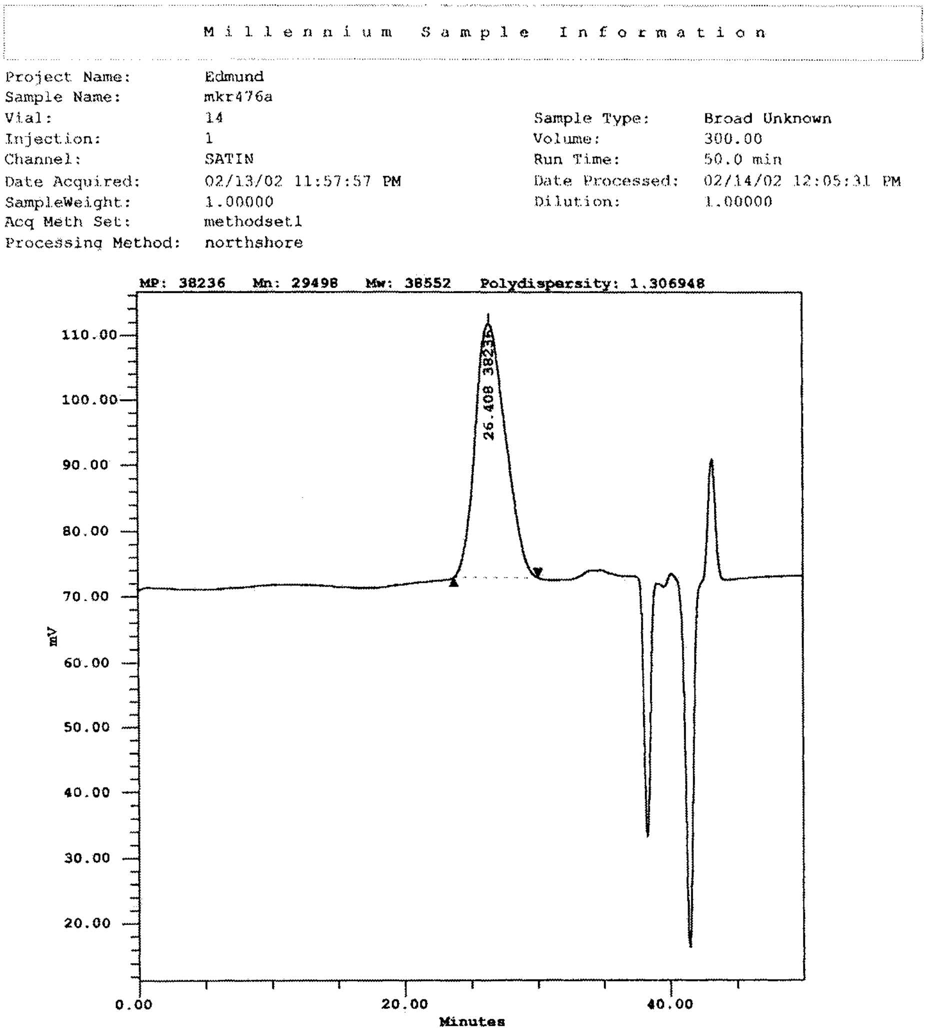
Millennium Sample Information

Project Name:	Edmund		
Sample Name:	mkr464		
Vial:	5	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	02/06/02 03:04:32 PM	Date Processed:	02/07/02 11:38:14 AM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		

MP: 31413 Mn: 28527 Mw: 43270 Polydispersity: 1.516843



G40



```
                    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:         Edmund
Sample Name:          mkr476a
Vial:                 14                           Sample Type:      Broad Unknown
Injection:            1                            Volume:           300.00
Channel:              SATIN                        Run Time:         50.0 min
Date Acquired:        02/13/02 11:57:57 PM         Date Processed:   02/14/02 12:05:31 PM
SampleWeight:         1.00000                      Dilution:         1.00000
Acq Meth Set:         methodset1
Processing Method:    northshore
```

MP: 38236   Mn: 29498   Mw: 38552   Polydispersity: 1.306948

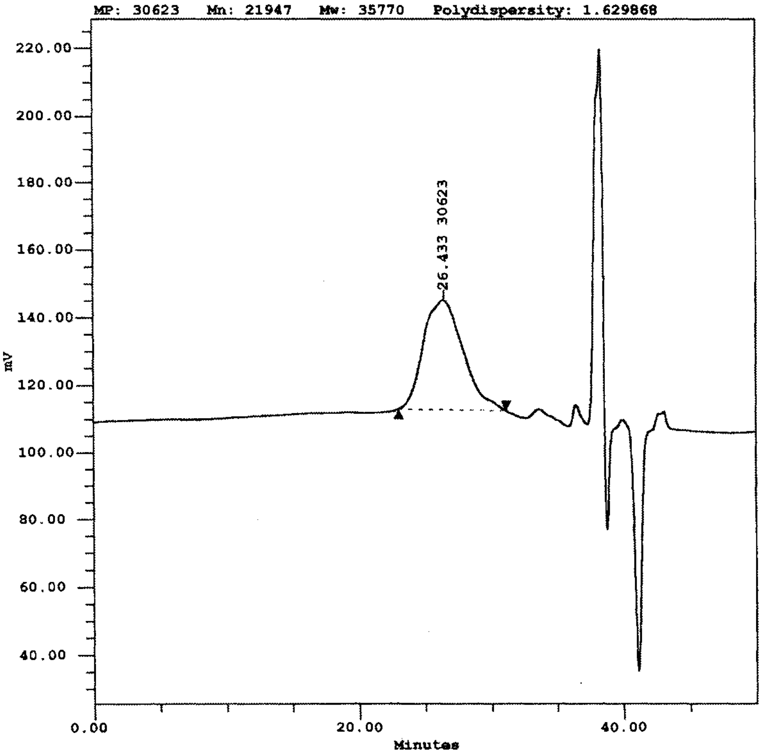
G41

Millennium Sample Information

Project Name: Edmund2
Sample Name: mkr484a
Vial: 2
Injection: 1
Channel: SATIN
Date Acquired: 03/14/02 06:14:01 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: Thunderbay

Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 03/15/02 01:57:40 PM
Dilution: 1.00000

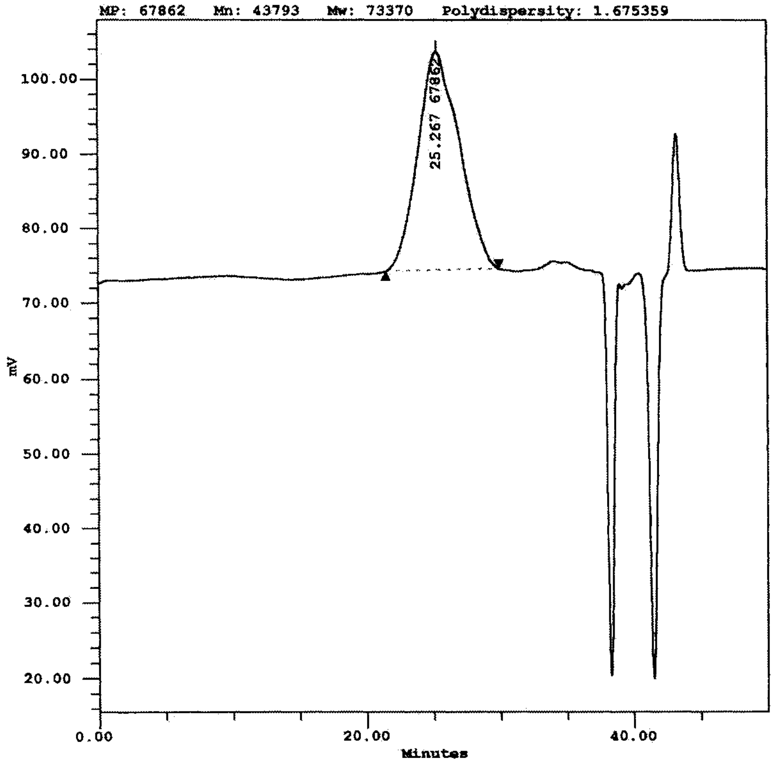
MP: 30623 Mn: 21947 Mw: 35770 Polydispersity: 1.629868



G42

Millennium Sample Information

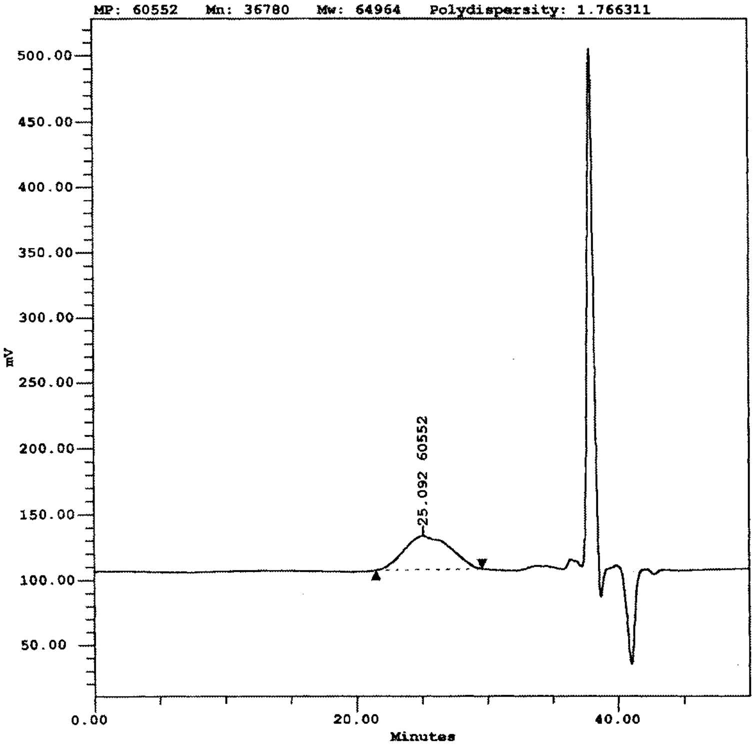
Project Name:	Edmund		
Sample Name:	mkr476b		
Vial:	15	Sample Type:	Broad Unknown
Injection:	1	Volume:	300.00
Channel:	SATIN	Run Time:	50.0 min
Date Acquired:	02/14/02 12:51:42 AM	Date Processed:	02/14/02 12:05:55 PM
SampleWeight:	1.00000	Dilution:	1.00000
Acq Meth Set:	methodset1		
Processing Method:	northshore		


MP: 67862 Mn: 43793 Mw: 73370 Polydispersity: 1.675359

G43

```
                    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:        Edmund2
Sample Name:         mkr484b
Vial:                3                         Sample Type:      Broad Unknown
Injection:           1                         Volume:           300.00
Channel:             SATIN                     Run Time:         50.0 min
Date Acquired:       03/14/02 07:07:43 PM      Date Processed:   03/15/02 01:58:11 PM
SampleWeight:        1.00000                   Dilution:         1.00000
Acq Meth Set:        methodset1
Processing Method:   Thunderbay
```

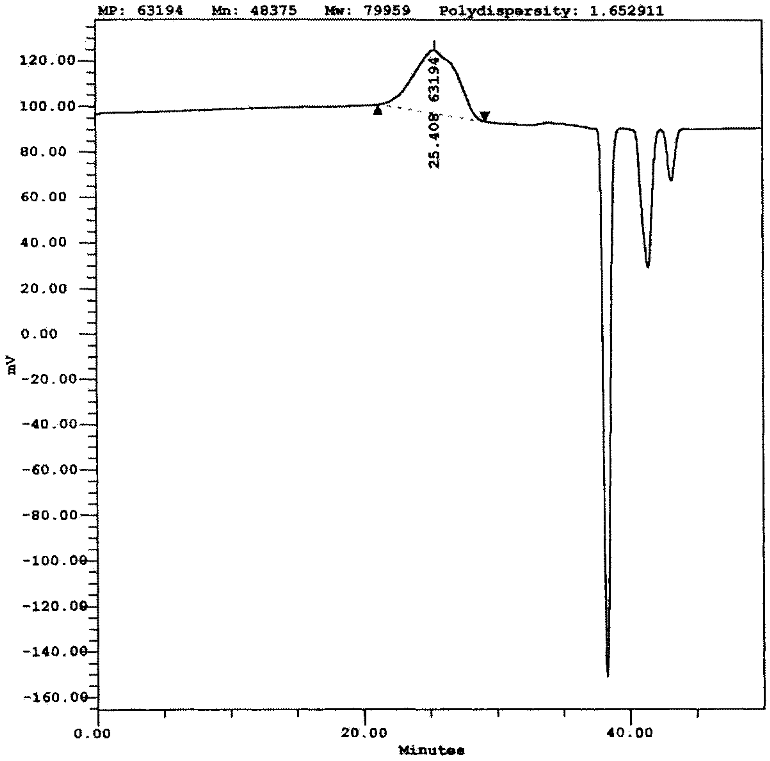


G44

Millennium Sample Information

Project Name: Edmund
Sample Name: mkr476c
Vial: 1
Injection: 3
Channel: SATIN
Date Acquired: 02/19/02 03:35:43 PM
SampleWeight: 1.00000
Acq Meth Set: methodset1
Processing Method: northshore
Sample Type: Broad Unknown
Volume: 300.00
Run Time: 50.0 min
Date Processed: 02/20/02 09:37:13 AM
Dilution: 1.00000

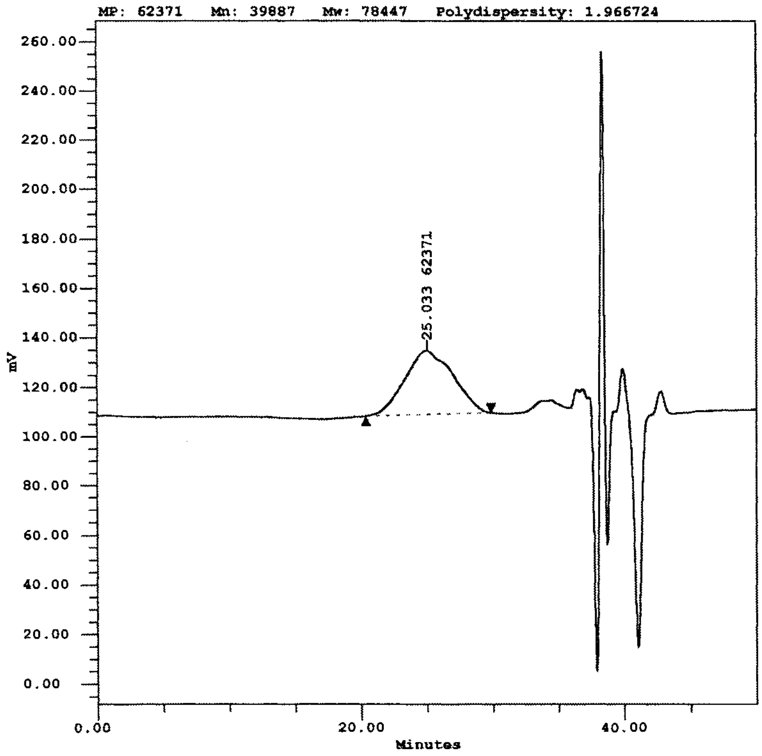
MP: 63194 Mn: 48375 Mw: 79959 Polydispersity: 1.652911



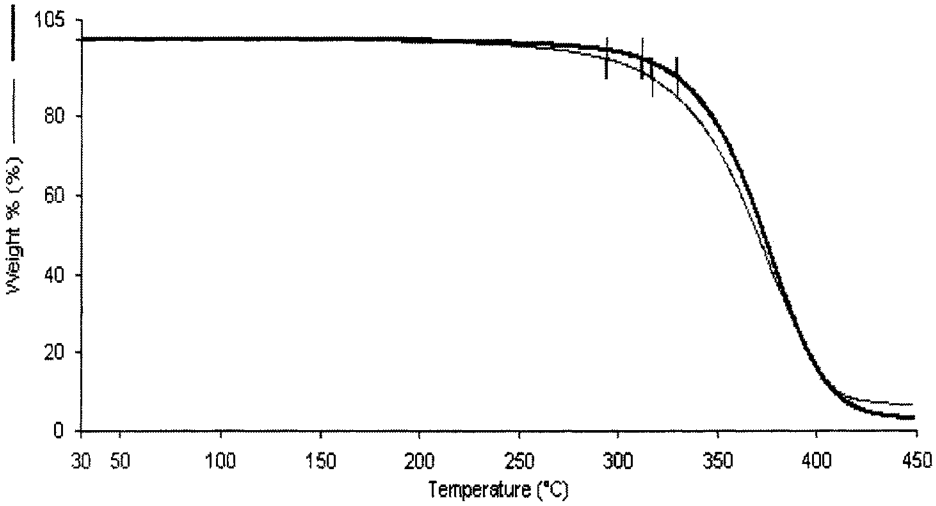
G45

```
                    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:          Edmund2
Sample Name:           mkr484c
Vial:                  4                             Sample Type:       Broad Unknown
Injection:             1                             Volume:            300.00
Channel:               SATIN                         Run Time:          50.0 min
Date Acquired:         03/14/02 08:01:26 PM          Date Processed:    03/15/02 01:58:32 PM
SampleWeight:          1.00000                       Dilution:          1.00000
Acq Meth Set:          methodset1
Processing Method:     Thunderbay
```

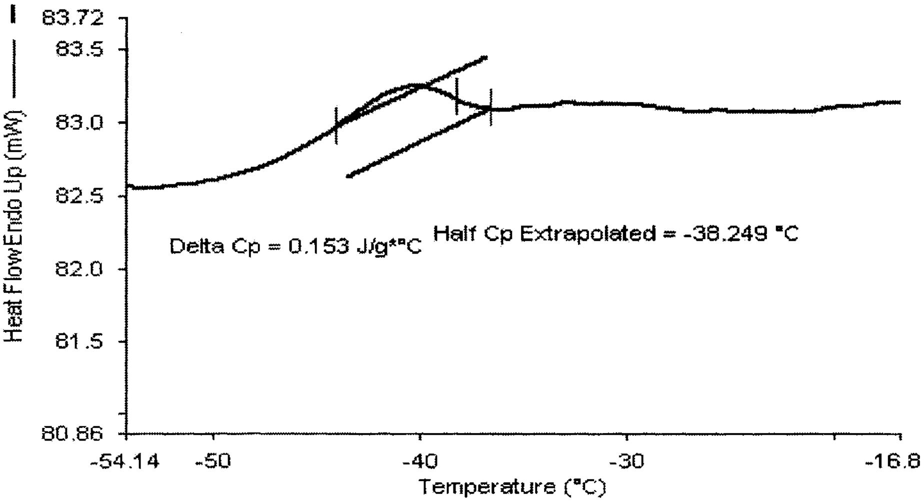


G46



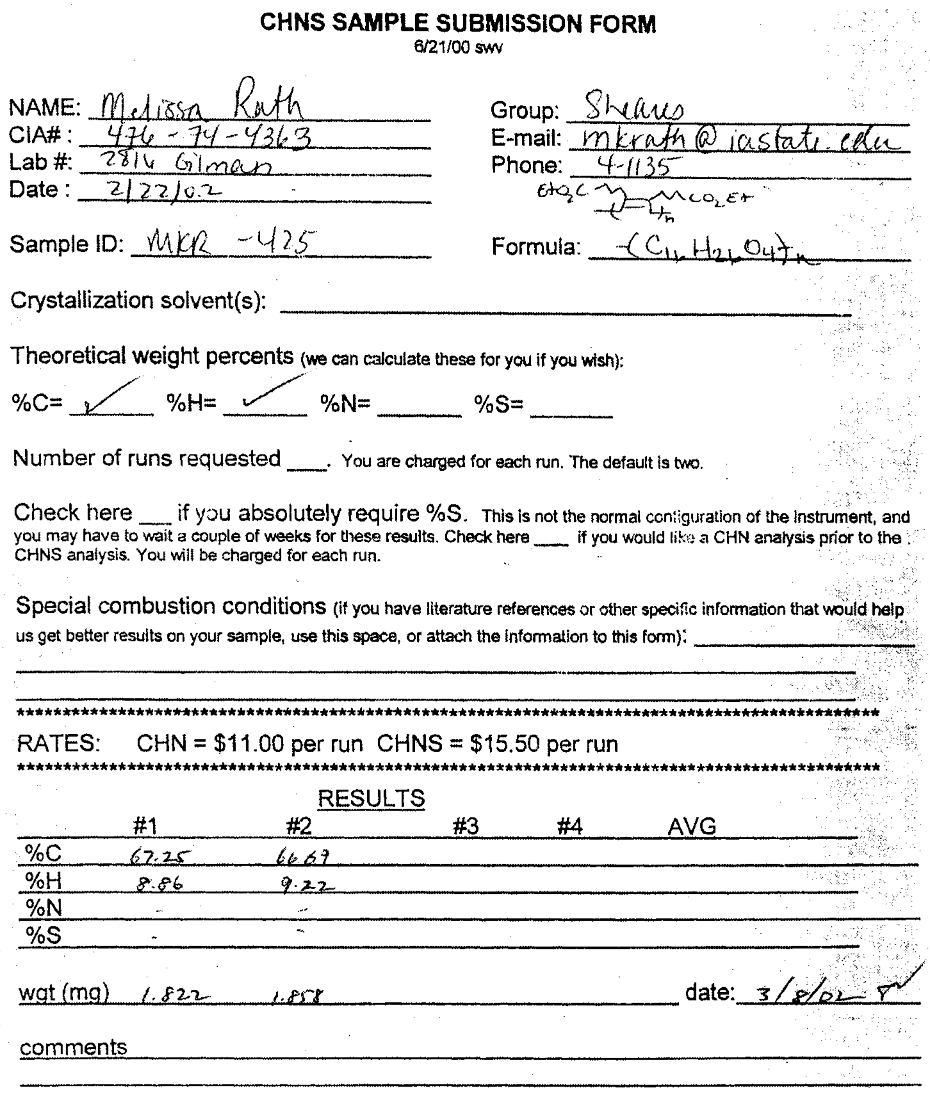
TGA12

TGA data for Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene]



D12

DSC data for Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene]



CHNS SAMPLE SUBMISSION FORM

6/21/00 swv

NAME: Melissa Rath
CIA# : 476-74-4363
Lab #: 2816 Gilman
Date : 2/22/02

Group: Shears
E-mail: mkrath@iastate.edu
Phone: 4-1135

Sample ID: MKR-425

Formula: $-(C_{11}H_{21}O_4)-_n$

Crystallization solvent(s): ________

Theoretical weight percents (we can calculate these for you if you wish):

%C= ✓ %H= ✓ %N= ____ %S= ____

Number of runs requested ____. You are charged for each run. The default is two.

Check here ___ if you absolutely require %S. This is not the normal configuration of the instrument, and you may have to wait a couple of weeks for these results. Check here ____ if you would like a CHN analysis prior to the CHNS analysis. You will be charged for each run.

Special combustion conditions (if you have literature references or other specific information that would help us get better results on your sample, use this space, or attach the information to this form): ________

****

RATES: CHN = \$11.00 per run CHNS = \$15.50 per run

****

RESULTS

	#1	#2	#3	#4	AVG
%C	67.25	66.69			
%H	8.86	9.22			
%N	-	-			
%S	-	-			

wgt (mg) 1.822 1.858 date: 3/8/02

comments ________

EA12

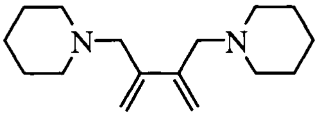
Elemental Analysis of Poly[2,3-bis(4-ethoxy-4-oxobutyl)-1,3-butadiene]

APPENDIX C1:

Synthesis of 2,3-bis(piperidinylmethyl)-1,3-butadiene

Introduction

In the recent years, our group has synthesized a number of *N,N*-dialkylaminoisoprenes.[1,2] The amines have been widely studied due to their chemical and structural versatility. By changing the substituents on the amine, one can change the properties exhibited by its polymer. For example, by polymerizing bulkier monomers significantly more *cis*-1,4 was formed.[3-5] These polymers have the unique ability to crosslink via ionic and covalent bonding. This makes them potentially useful for ionomers, which can then be used in applications such as membranes, packagings, adhesives and dispersants. Stadler has explored many dialkylaminoisoprenes including 2-piperidinylmethyl-1,3-butadiene.[3-5] Our group is interested in taking these dialkylaminoisoprenes one step further to the disubstituted 1,3-butadienes. By synthesizing a disubstituted monomer corresponding to each dialkylaminoisoprene, we plan to compare the polymer properties resulting from each of these monomers. Through the polymerization of the functionalized disubstituted butadiene we hope to achieve an enhancement of the properties that make the amines interesting. We have successfully synthesized a new monomer, 2,3-bis(piperidinylmethyl)-1,3-butadiene (**I**), which is the first of the amine functionalized disubstituted 1,3-butadienes to be made.



I

Experimental

Materials

All reagents were purchased from Aldrich and used as received except when reported. Acetonitrile was distilled prior to use. 2,3-Bis(piperidinylmethyl)-1,3-butadiene was purified by distillation and recrystallization until the ^{1}H NMR corresponded to the expected structure.

Synthetic Procedures

Synthesis of 2,3-Bis(piperidylmethyl)-1,3-butadiene.

2,3-Bis(chloromethyl)-1,3-butadiene.[6] Anhydrous copper(II) chloride (53.8 g, 400 mmol), palladium (II) chloride (0.130 g, 0.5 mmol) and acetonitrile (160 mL) were added to a 500 mL, teflon-stoppered round bottom flask with vigorous stirring. After three freeze-pump-thaw cycles, allene (10.0 g, 250 mmol) was condensed into the reaction flask at –78 °C. The reaction was allowed to warm to room temperature while stirring for 24 hours. The resulting brown mixture was poured into 200 mL ether and filtered to remove the black precipitate. The filtrate was concentrated using the rotary evaporator and diluted with 100 mL of ether to remove the remaining brown precipitate. The solution was again concentrated via the rotary evaporator to yield a dark brown solid. The solid was dissolved in *n*-pentane and filtered through silica gel in a sintered glass funnel. Upon concentration, 2,3-bis(chloromethyl)-1,3-butadiene was obtained as a white solid in 95 %yield (35 g, 237 mmol). ^{1}H NMR (**N20**), ($CDCl_3$): δ 4.27 (s, 4H; $-C\underline{H}_2Cl$), 5.48 (s, 2H; $=C\underline{H}$), 5.49 (s, 2H; $=C\underline{H}$). ^{13}C NMR (**N21**), ($CDCl_3$): δ 45.8 ($\underline{C}H_2Cl$), 119 ($=\underline{C}H_2$), 141 ($-\underline{C}=C$).

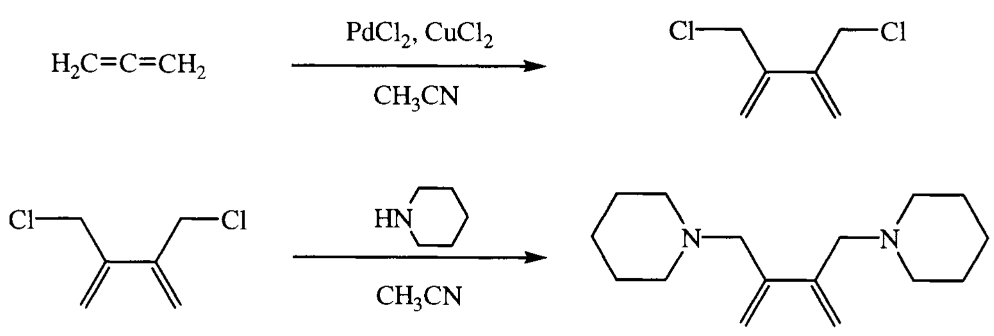
2,3-Bis(piperidinylmethyl)-1,3-butadiene. 2,3-Bis(chloromethyl)-1,3-butadiene (41.9 g, 278 mmol) was dissolved in 250 mL of acetonitrile in a 500 mL round bottom flask. Piperidine (65.5 mL, 56.3 g, 662 mmol) was added dropwise to the mixture and allowed to stir for 1 hour. The mixture then was added to 45 mL of piperidine (38.6 g, 454 mmol) with 200 mL of acetonitrile in a 1000 mL round bottom flask and was allowed to stir for 12 hours at room temperature. Following this, a sodium hydroxide solution (25 g in 150 mL) was added to the flask to dissolve the piperidyl salt crystals that were formed during the reaction. The acetonitrile was then removed using the rotary evaporator to obtain some white crystals and then the mixture was placed in the refrigerator overnight to allow more crystals to come out of solution. The mixture was then distilled under vacuum and 500 mL of water was added to the distillate. The resulting solution was placed in the refrigerator overnight, filtered and dried under vacuum to result in 22% yield (15.4 g, 62 mmol) in greater than 99% purity by GC/MS (**M5**). ^{1}H NMR (**N22**), ($CDCl_3$): δ 1.4 (m, 2H; -C$\underline{H}_2$), 1.55 (m, 4H; -C$\underline{H}_2$), 2.3 (m, 4H; C$\underline{H}_2$N), 3.0 (s, 2H, NC$\underline{H}_2$-C=), 5.05 (s, 2H; =C$\underline{H}$), 5.27 (s, 2H; =C$\underline{H}$). ^{13}C NMR (**N23**), ($CDCl_3$): δ 25 (-$\underline{C}H_2$), 27 (-$\underline{C}H_2$), 55 (-$\underline{C}H_2$N), 63 (N$\underline{C}H_2$-C=), 115 (=$\underline{C}H_2$), 145 (-$\underline{C}$ =). High-resolution mass spectrometry (**M6**): theoretical mass 248.22525, measured mass 248.22566, deviation 1.7 ppm.

RESULTS AND DISCUSSION

The synthesis of 2,3-bis(piperidinylmethyl)-1,3-butadiene is an efficient synthesis that could also be used to make a number of different disubstituted 1,3-butadienes. It is the versatile product, 2,3-bis(chloromethyl)-1,3-butadiene, from the first step that can undergo different S_N2 reactions that has the potential to form a variety of functionalized disubstituted

1,3-butadienes. The resulting monomer was made in low yield (22%) with high purity through this two-step synthesis.

The first step of this synthesis involved forming the π-allyl palladium complex with allene that was then oxidatively cleaved by treatment of copper (II) chloride to 2,3-bis(chloromethyl)-1,3-butadiene in 95% crude yield and 70% pure yield. The 2,3-bis(chloromethyl)-1,3-butadiene was purified by column chromatography to produce clean white crystals. The second reaction displaces the chlorine with the piperidine group via an S_N2 reaction to produce 2,3-bis(piperidinylmethyl)-1,3-butadiene in 24% yield. The resulting product was a solid, which was then purified by distilling off the excess amine and recrystallization in water. This synthesis is shown in Scheme 1. The monomer was characterized by ^1H NMR (**N22**) and ^{13}C NMR (**N23**) and was found to be greater than 99% pure by GC/MS (**M5**). High resolution mass spectrometry also verified that 2,3-bis(piperidinylmethyl)-1,3-butadiene had a deviation of 1.7 ppm (**M6**). These monomers were chosen because of their potential applications in adhesives, packagings and coatings as well. The piperidyl group has a unique feature; it has the groups tied back from the nitrogen that allows the unshared pair of electrons to be more exposed. This might help to quaternize the amine, thus making the polar monomer water soluble and increasing the ability to be utilized as an ionomer. The polar groups should also increase the attractive forces between the chains upon polymerization, thus increasing the T_g and thermal stability. These same forces should also increase the adhesion properties between the polymer and various surfaces.



Scheme 1. Synthesis of 2,3-Bis(piperidinylmethyl)-1,3-butadiene.

By using a disubstituted monomer we can double the functionality within a given repeat unit. This should allow us to diminish the actual number of functionalized repeat units within the polymer while maintaining the same effect from the functionality. The other feature resulting from the disubstituted monomer is in the resulting microstructure of the polymer. Many of the monosubstituted 1,3-butadienes exhibit *cis* and *trans* microstructure as well as 1,2 and 3,4 microstructure in the polymer. With the disubstituted monomers, our group has previously shown that only 1,4-microstructure was produced upon polymerization. All of these aspects make these disubstituted functionalized 1,3-butadienes good candidates for tailoring polymers to the desired application.

CONCLUSIONS

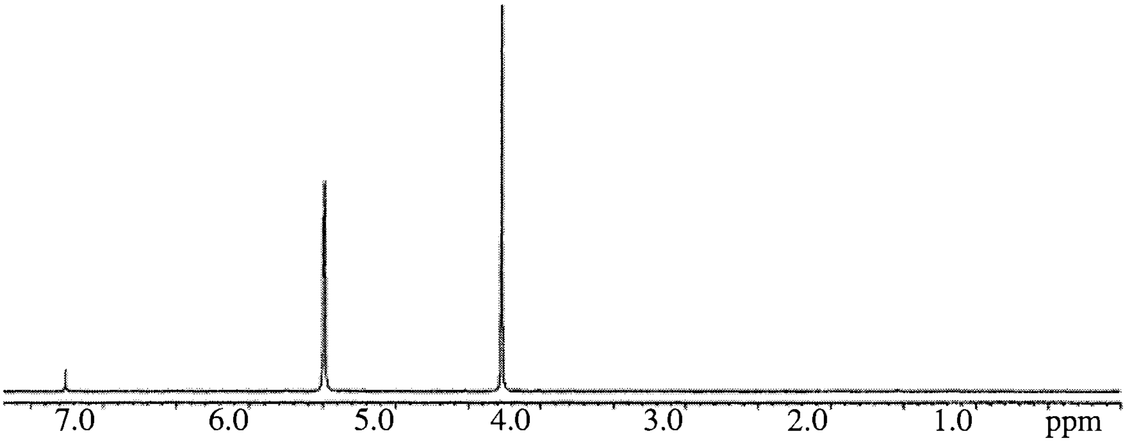
In a palladium catalyzed synthesis followed by an S_N2 reaction, 2,3-bis(piperidinylmethyl)-1,3-butadiene was made. This monomer was produced in low yield and high purity. Upon polymerization, materials made with this monomer should have potential applications in adhesives, packagings, coatings and ionomers.

REFERENCES

1. Sheares, V. V.; Wu, L.; Li, Y.; Emmick, T. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **2000,** *38*, 4070.
2. Wu, L; Sheares, V. V. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3227.
3. Petzhold, C.; Stadler, R.; Frauenrath, H. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 33.
4. Petzhold, C.; Morschhauser, R.; Kolshorn, H.; Stadler, R. *Macromolecules* **1994**, *27*, 3708.
5. Petzhold, C.; Stadler, R. *Macromol. Chem. Phys.* **1995**, *196*, 2625.
6. Hegedus, L.; Kambe, N.; Ishii, Y.; Mori, A *J. Org. Chem.* **1985**, *50*, 2240.

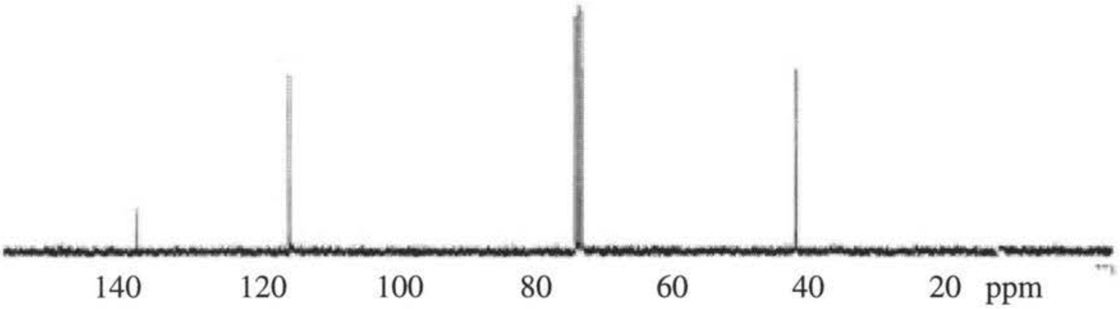
APPENDIX C2:

Appendix C1 Data



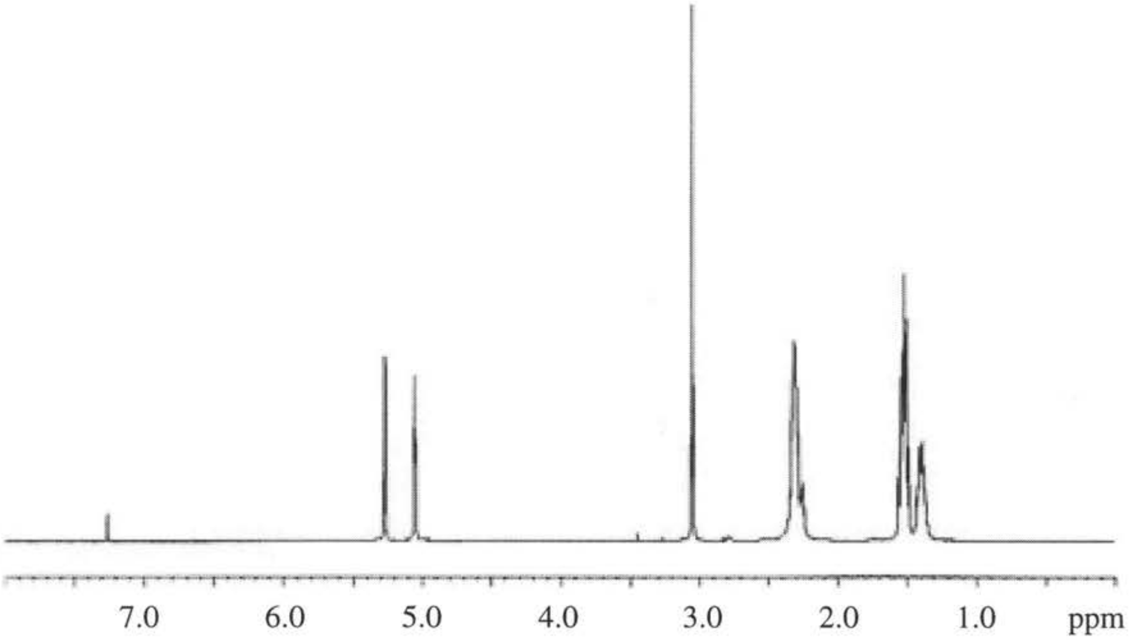
N20

2,3-Bis(chloromethyl)-1,3-butadiene ($CDCl_3$)



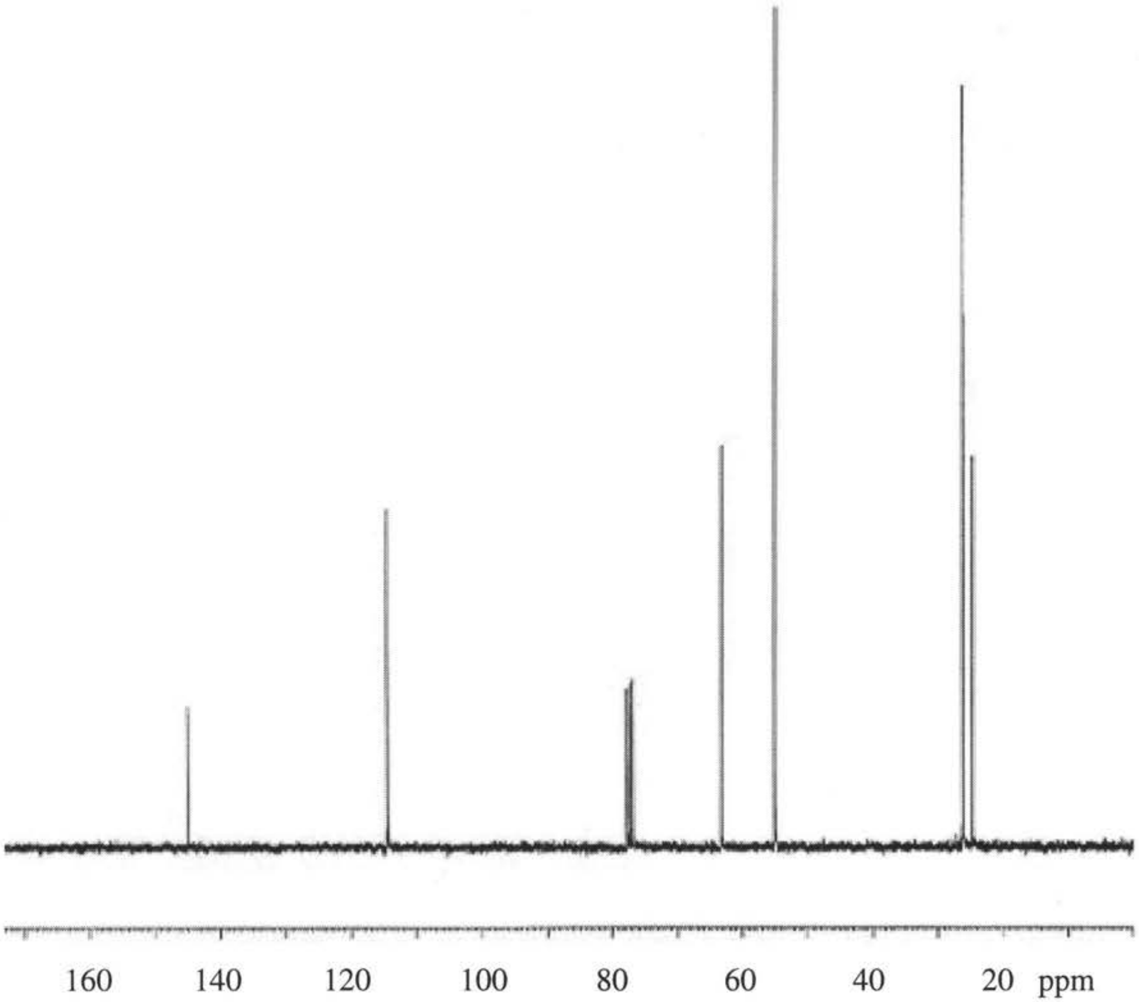
N21

2,3-Bis(chloromethyl)-1,3-butadiene (^{13}C, $CDCl_3$)



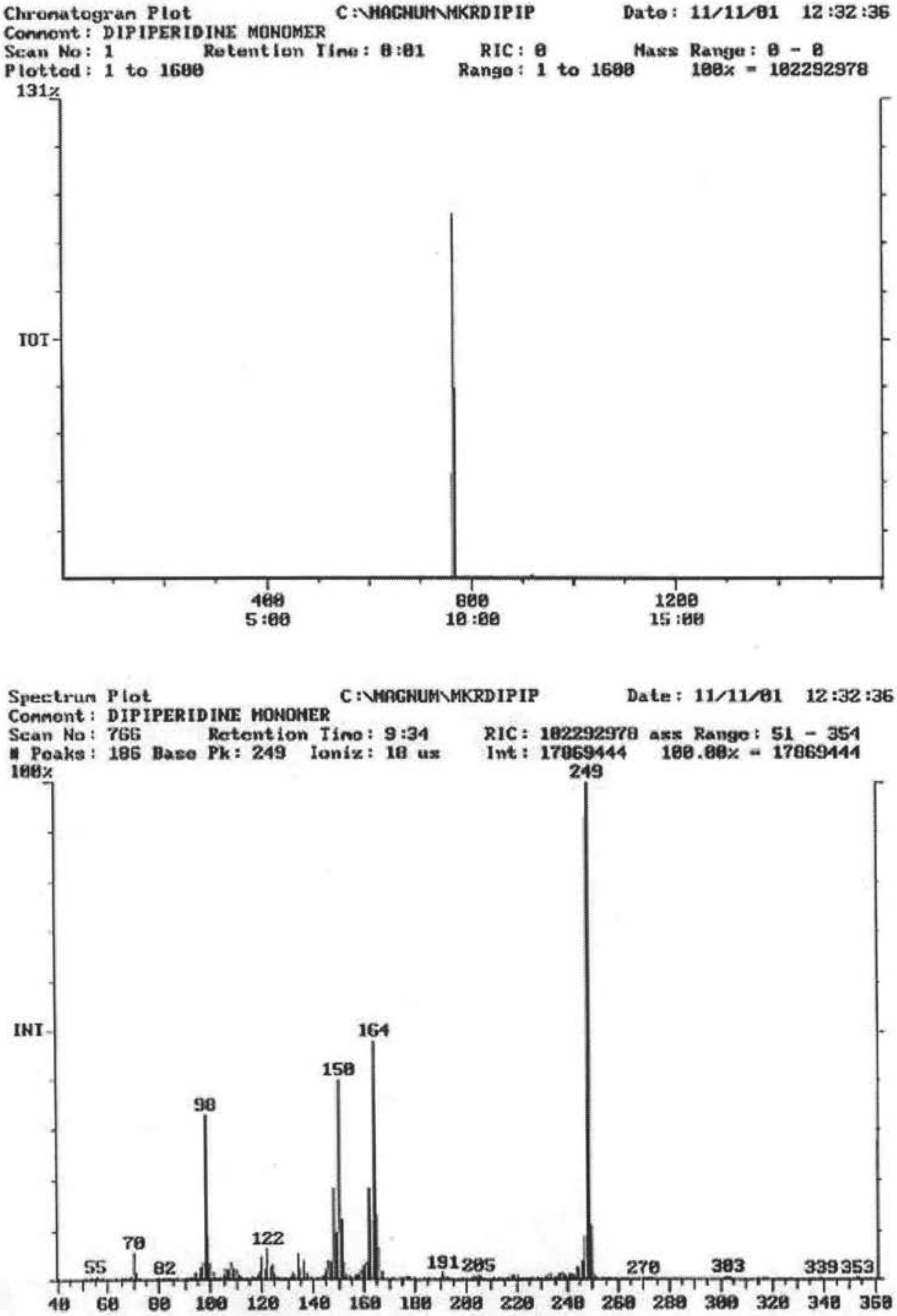
N22

2,3-Bis(piperidinylmethyl)-1,3-butadiene ($CDCl_3$)



N23

2,3-Bis(piperidinylmethyl)-1,3-butadiene (^{13}C, CDCl$_3$)



Chromatogram Plot C:\MAGNUM\MKRDIPIP Date: 11/11/01 12:32:36
Comment: DIPIPERIDINE MONOMER
Scan No: 1 Retention Time: 0:01 RIC: 0 Mass Range: 0 - 0
Plotted: 1 to 1600 Range: 1 to 1600 100% = 102292978

Spectrum Plot C:\MAGNUM\MKRDIPIP Date: 11/11/01 12:32:36
Comment: DIPIPERIDINE MONOMER
Scan No: 766 Retention Time: 9:34 RIC: 102292978 ass Range: 51 - 354
Peaks: 186 Base Pk: 249 Ioniz: 10 us Int: 17069444 100.00% = 17069444

M5

GC-MS chromatograph of 2,3-bis(piperidylmethyl)-1,3-butadiene

Manual Peak Matching Report
For Accurate Mass Determination

Theoretical mass	Experimental mass	PFK matching mass	Deviation*
248.22525	248.22566	242.98562	1.7 ppm

* The deviation is obtained from the following equation:

$$\text{deviation}=\frac{\text{experimental mass - theoretical mass}}{\text{nominal mass}}$$

Where nominal mass takes in account only ^{12}C, ^{1}H, ^{16}O, ^{14}N etc...

Theoretical mass correspond to the mass of the most abundant isotope peak

M6

High resolution mass spectrometry of 2,3-bis(piperidylmethyl)-1,3-butadiene