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ISOMERIC POLY(BENZOPHENONE)S: SYNTHESIS OF HIGHLY CRYSTALLINE POLY(4,4'-BENZOPHENONE) AND AMORPHOUS POLY(2,5-BENZOPHENONE), A SOLUBLE POLY(p-PHENYLENE) DERIVATIVE

BY

R.W. PHILLIPS, V.V. SHEARES, E.T. SAMULSKI, J.M. DESIMONE*

DEPARTMENT OF CHEMISTRY
CB #3290 VENABLE & KENAN LABS
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NC 27599-3290

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R.W. Phillips, V.V. Sheares, E.T. Samulski, J.M. DeSimone*

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
University of North Carolina
CB #3290 Venable & Kenan Labs
Chapel Hill, NC 27599-3290

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Nickel-catalyzed polymerization which employs the coupling of isomeric dichlorobenzophenones is described. The polymerization utilizes inexpensive readily available monomers, 4,4'-dichlorobenzophenone (4,4'-DCBP) and 2,5-dichlorobenzophenone (2,5-DCBP). The poly(4,4'-benzophenone) can be derivatized to be soluble during the synthesis by the use of a ketimine precursor that is subsequently hydrolyzed to give the target material. The polymerization of 2,5-dichlorobenzophenone yields a soluble derivative of poly(p-phenylene). The resulting polymers were characterized to confirm the composition, molar mass, and thermal properties. The Ni(0) catalyzed route proves to be facile and economically feasible and opens the way to a large variety of heterocyclic and phenyl-based homo- and copolymers.

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Isomeric Poly(benzophenone)s: Synthesis of Highly Crystalline Poly(4,4'-benzophenone) and Amorphous Poly(2,5-benzophenone), A Soluble Poly(*p*-phenylene) Derivative

R.W. Phillips, V.V. Sheares, E.T. Samulski, J.M. DeSimone*

Department of Chemistry
University of North Carolina at Chapel Hill
Kenan and Venable Laboratories
Chapel Hill, N.C. 27599-3290

Abstract.

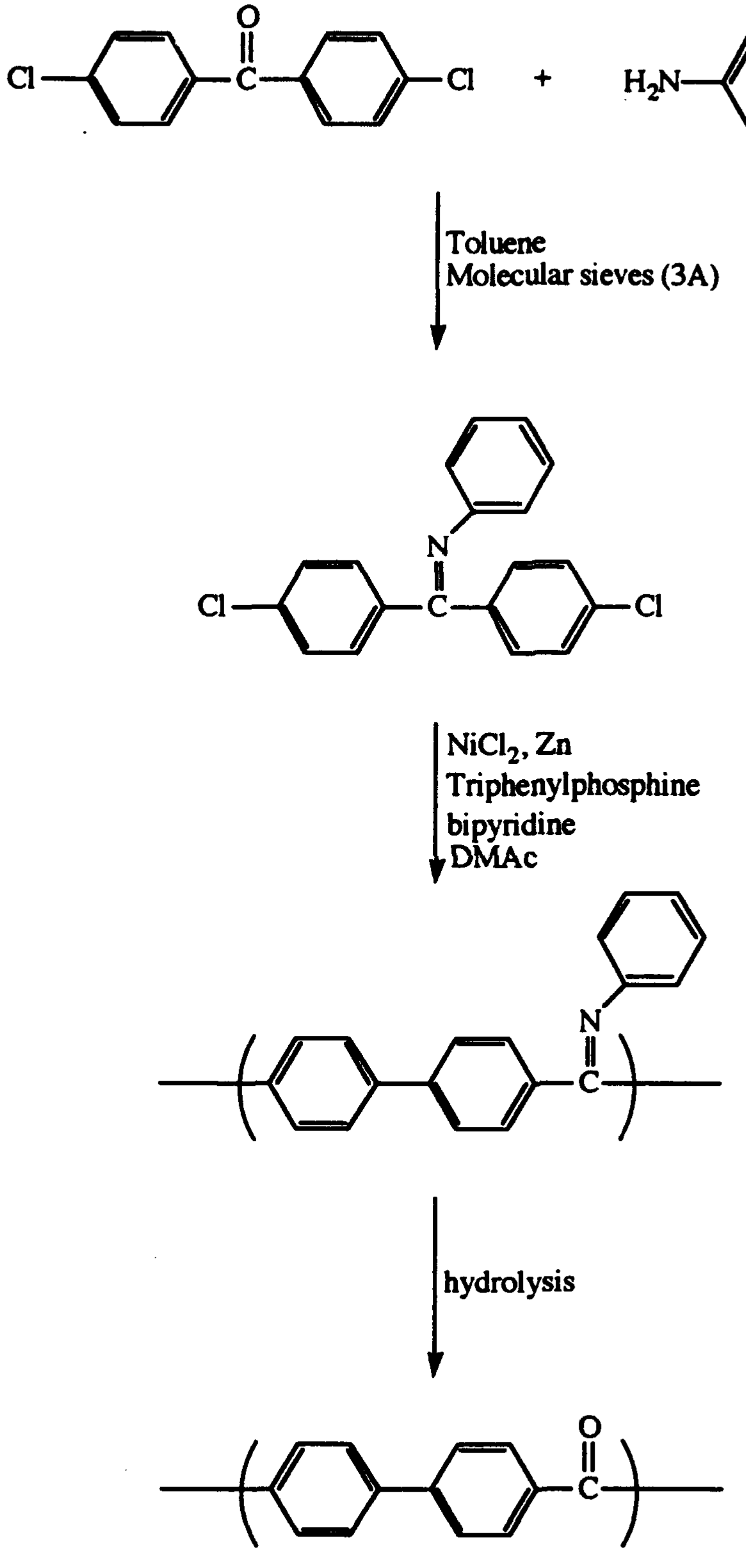
Nickel-catalyzed polymerization which employs the coupling of isomeric dichlorobenzophenones is described. The polymerization utilizes inexpensive readily available monomers, 4,4'-dichlorobenzophenone (4,4'-DCBP) and 2,5-dichlorobenzophenone (2,5-DCBP). The poly(4,4'-benzophenone) can be derivatized to be soluble during the synthesis by the use of a ketimine precursor that is subsequently hydrolyzed to give the target material. The polymerization of 2,5-dichlorobenzophenone yields a soluble derivative of poly(*p*-phenylene). The resulting polymers were characterized to confirm the composition, molar mass, and thermal properties. The Ni(0) catalyzed route proves to be facile and economically feasible and opens the way to a large variety of heterocyclic and phenyl-based homo- and copolymers.

Herein we describe a nickel-catalyzed polymerization which employs the coupling of bis(arylhalide)s as the polymer-forming reaction in a step growth polymerization of isomeric dichlorobenzophenones. The reaction utilized has general applicability to the synthesis of new processable engineering resins of superior thermal stability. The synthetic approach was first demonstrated by Colon *et. al.*[1] in the synthesis of biphenyl. They found that a Ni(0)-catalyzed system would quantitatively convert chlorobenzene to biphenyl in short times at mild temperatures. It was thought that since the coupling of aryl chlorides could be achieved in high yields, the possibility existed for the use of this catalyst as a route to high polymer by coupling difunctional monomers. Poly(ether ether sulfone)s[2] were chosen by Colon as the first system to be studied because they are generally amorphous and soluble in dipolar aprotic solvents such as N,N-dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidinone (NMP) at the relatively low temperatures (70 °C) required to produce high polymer. Further studies of this system,[3] in addition to a variety of poly(arylene ether ketone)s, have been investigated by Ueda *et al.*[4] Ueda utilized Ni(0) coupling of aromatic dichlorides containing ether-ketone structures to prepare high molecular weight poly(arylene ether ketone)s. This method proved advantageous compared with conventional methods because of the high rates and the mild conditions of the reaction.

Recently, Percec extended the use of this catalyst system in an attempt to synthesize soluble poly(phenylene)s.[5] Percec's efforts in the design of soluble materials were focused on the polymerization of "crankshaft" type monomers. Specifically, they reported the synthesis of Ni(0)-catalyzed oligomerization of 4,4'''-dichloroquaterphenyls. In spite of the fact that the kink was introduced, molecular weight was still limited due to poor solubility ($<Mn> = 9.0 \times 10^2$ g/mol).

As is well known, poly(*p*-phenylene) (PPP) exhibits remarkable thermal stabilities. They have been considered for use in numerous thermally robust organic materials including composites, lubricant additives and thermoset precursors for high performance aerospace materials applications. The improvement of the solubility of poly(phenylene) has been attempted by attaching lateral substituents.[6,7] Appropriately substituted materials should be soluble and yet exhibit thermal properties comparable to that of PPP. Several researchers have examined the substitution of PPP via polymerization techniques other than Ni(0) catalysis to vary polymer properties. Schluter *et.al.*[8,9] have described the palladium-catalyzed polymerization of alkyl-substituted poly(*p*-phenylene) derivatives. In some cases, degrees of polymerization of 30 to 50 could be achieved and solubility be maintained. Tour has also investigated the substitution of a PPP backbone, but with the goal of making thermoset precursors.[10] Specifically, they reported the functionalization of brominated PPP with several alkynes. A tetrahydrofuran promoted polymerization of bromo-lithiobenzene gave the polymer and subsequent replacement of the bromines with alkynes led to the target materials. Novak has focused on the synthesis of water soluble poly(*p*-quaterphenylene 2,2'-dicarboxylate) via the palladium-mediated cross-coupling of aryl halides and arylboronic acids.[11] The resulting polymers[12] are rodlike polyelectrolytes that have the unusual properties of water solubility, conformational rigidity, and charged character similar to biopolymers. More recently, Morrocco reported the physical properties of soluble poly(*p*-phenylene) derivatives.[13] The synthetic details were not disclosed, but it was suggested that the "route involves relatively inexpensive materials". These substituted poly(*p*-phenylene)s were reported to be soluble in common organic solvents and exhibit numerous interesting properties which make them candidates for high performance applications. Herein, we report the synthesis of isomeric poly(benzophenone)s using Ni(0) catalysts for the polymerization of inexpensive, readily available monomers, 4,4'-dichlorobenzophenone (4,4'-DCBP) and 2,5-dichlorobenzophenone (2,5-DCBP).

The first polymerization was attempted using 4,4'-dichlorobenzophenone in N,N-dimethylacetamide (DMAc). Realizing that the 4,4'-DCBP would give a rigid, insoluble material, polymerization was accomplished through a ketimine derivative— a methodology derived by McGrath *et. al.*[14] for the synthesis of amorphous poly(arylene ether ketone)s. For our purposes, the required ketimine functional dichloride monomer (I) was synthesized by the treatment of 4,4'-DCBP with aniline in the presence of molecular sieves to give a bright yellow product in 50 % yield. After two recrystallizations from toluene, the purity of **I** was >99.9% by gas chromatography. The polymerization was then performed using the Ni(0) catalyst prepared from $NiCl_2$ (0.3125 moles), triphenylphosphine (0.0093 moles), bipyridine (0.3886 moles) and zinc dust (0.0495 moles) in DMAc. The monomer was dissolved in DMAc, added to the active catalyst (as evidenced by the deep red color) and stirred at 80 °C for 24 h. The resulting polymer (II)[15] was soluble in DMAc and gave an inherent viscosity of 0.25 dL/g (NMP, 30 °C). When this polymerization was repeated in 1-methyl-2-pyrrolidinone (NMP), an increase in inherent viscosity was seen (0.36 dL/g ; NMP at 30 °C) presumably due to the increased solubility in NMP. The amorphous polymer had a glass transition temperature of 225 °C with a 5% weight loss temperature in nitrogen at 558 °C. The amorphous prepolymer was hydrolyzed in 10% hydrochloric acid solution to generate poly(4,4'-benzophenone) (III) which is completely insoluble presumably due to high levels of crystallinity.[16] The 5% weight loss temperatures in air and nitrogen were 510 °C and 560 °C, respectively (Figure 1).

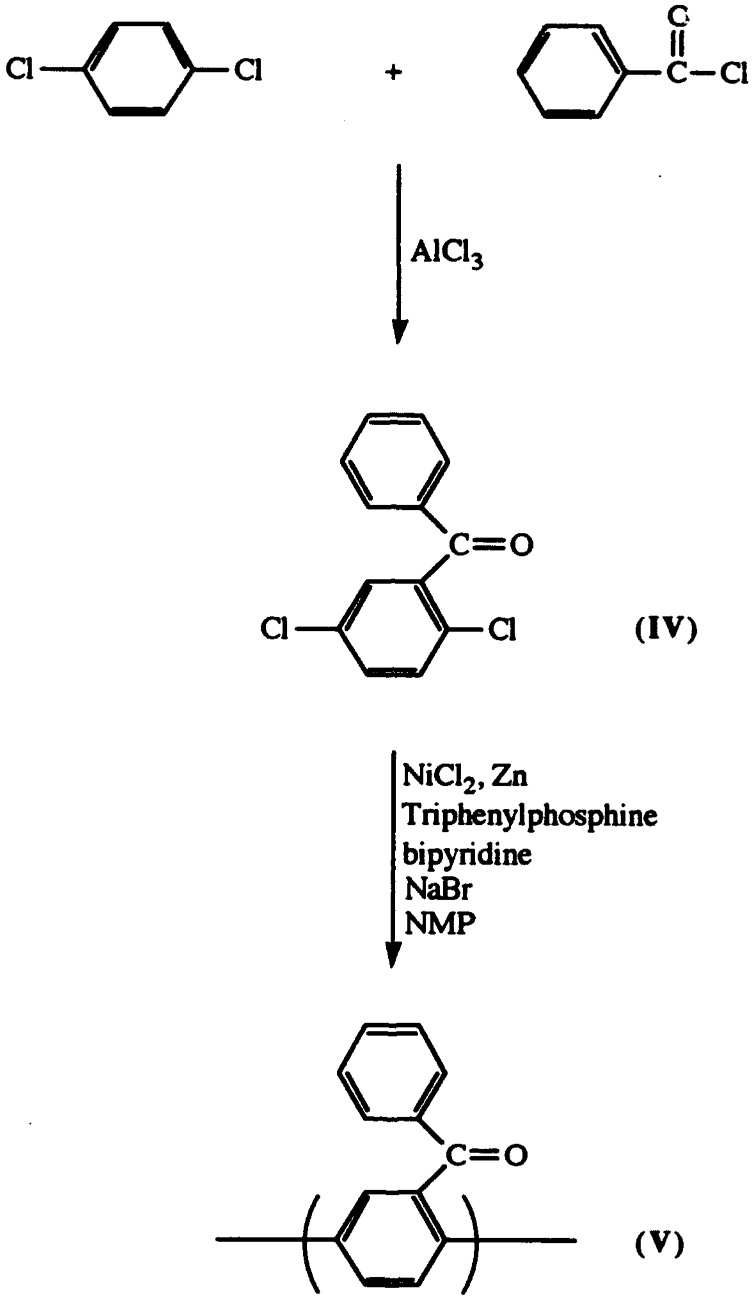


(I)

(II)

(III)

Synthesis of poly(2,5-benzophenone) not only increases the solubility of the polymer compared with the poly(4,4'-benzophenone), but also changes the polymer backbone to a substituted poly(*p*-phenylene). Synthesis of the monomer (**IV**) was accomplished by an aluminum chloride catalyzed acylation of benzoyl chloride and *p*-dichlorobenzene in a 1:1 ratio. The reaction was followed by TLC and complete conversion was seen after 3 h. Recrystallization from ethanol gave polymer grade monomer[17] (>99.9% purity by GC) that was analyzed extensively by a series of 2D NMR experiments to verify the correct isomer and rule out the possibility of halogen exchange during acylation. Once 2D NMR experiments confirmed the structure, the ^{13}C could be utilized to identify subsequent reaction products.[18] For this polymerization, we referred to Colon's original paper in which he described the quantitative synthesis of biphenyl from chlorobenzene. It was noted that the addition of an alkali metal salt to the reaction in one to three equivalents decreased the total reaction time from 2 h to 20 minutes. Upon addition of one equivalent of sodium bromide to the polymerization and the use of an overhead stirrer, high molar mass polymer was obtained (**V**).



The resulting light yellow material was characterized by a number of techniques in order to confirm composition and molar mass. The molar mass was analyzed by GPC giving a <Mn> = 12.4 x 10^3 g/mol[19] (Figure 2). Poly(2,5-benzophenone) has a Tg = 219 °C and

5% weight loss temperatures in air and in nitrogen of 496 °C and 495 °C, respectively (Figure 3).

In conclusion, it is apparent that use of the Ni(0) catalysts in polymerization of bis(aryl chloride)s leads to high molar mass polymers. In the case of poly(4,4'-benzophenone), the ketimine derivatized monomer gave increased solubilities resulting in higher molar mass. The successful polymerization of 2,5-DCBP yields a soluble derivative of poly(*p*-phenylene). Further work to increase the conversion, and therefore the molecular weight of the polymer in addition to more in-depth thermal analysis is underway. This Ni(0)-catalyzed polymerization is a facile and economically feasible synthetic route and opens the way to a low temperature, mild reaction for a large variety of heterocyclic and phenyl-based homopolymers. Moreover, the ability to make a wide range of copolymers enables one to tailor make polymers that will be generally applicable for utilization as advanced materials.

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15) The polymer was isolated by hot filtration to remove the zinc and precipitation into acetone to remove other remaining catalyst components.

16) WAXS analysis of polymer (III) is currently underway.

17) M.p. = 88.9 °C; MS, M^+ = 251 g/mol.

18) ^{13}C NMR of 2,5-DCBP: ∂140(C-1); ∂133(C-2); ∂131.1(C-3); ∂128.9(C-4); ∂129.2(C-5); ∂131.3(C-6); ∂136.2(C-1'); ∂130.1(C-2'); ∂128.8(C-3'); ∂134.1(C-4'); ∂128.8(C-5'); ∂130.1(C-6'); ∂190(C-carbonyl).

19) Determined by using a Water 717 GPC in methylene chloride using polystyrene standards.

Figure Captions

Figure 1. Thermal gravimetric analysis (TGA) thermograms of poly(4,4' benzophenone) (III) using a heating rate of 10 °C/min.

Figure 2. Size exclusion chromatogram of poly(2,5-benzophenone) (V) in CH_2Cl_2 (1 mL/min.) using a refractive index detector at 30 °C.

Figure 3. Thermal gravimetric analysis (TGA) thermograms of poly(2,5-benzophenone) (V) using a heating rate of 10 °C/min.

Figure 1.

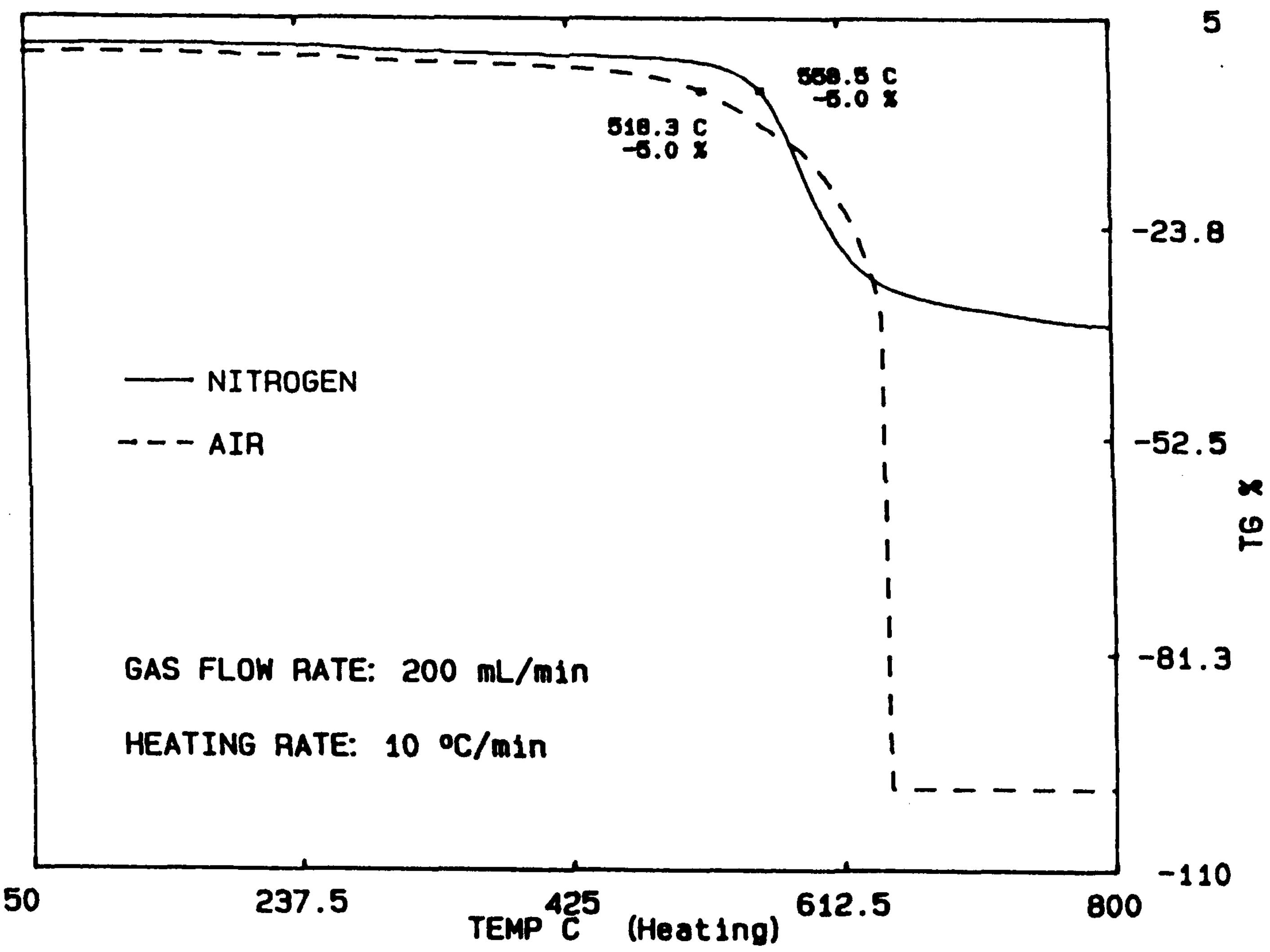
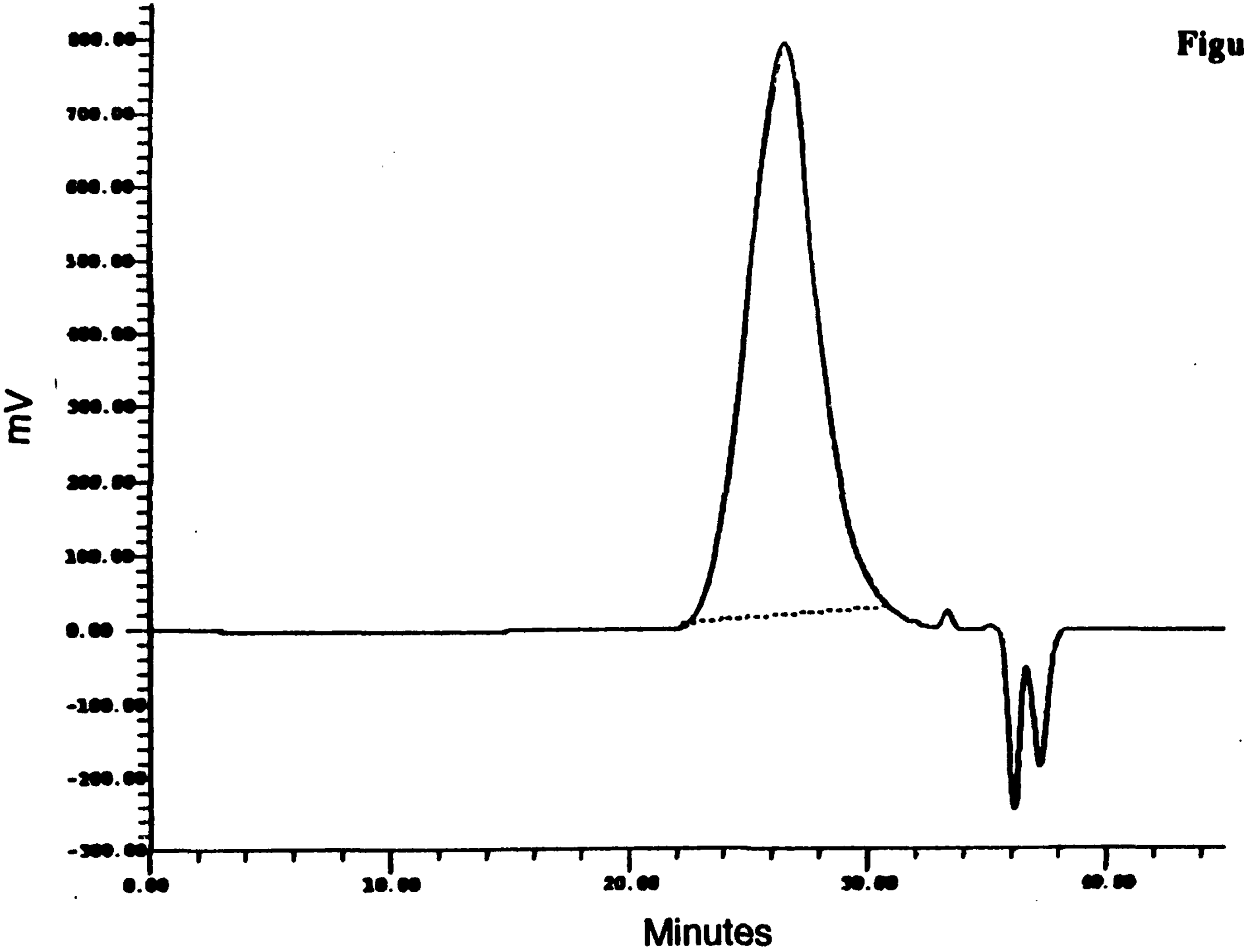
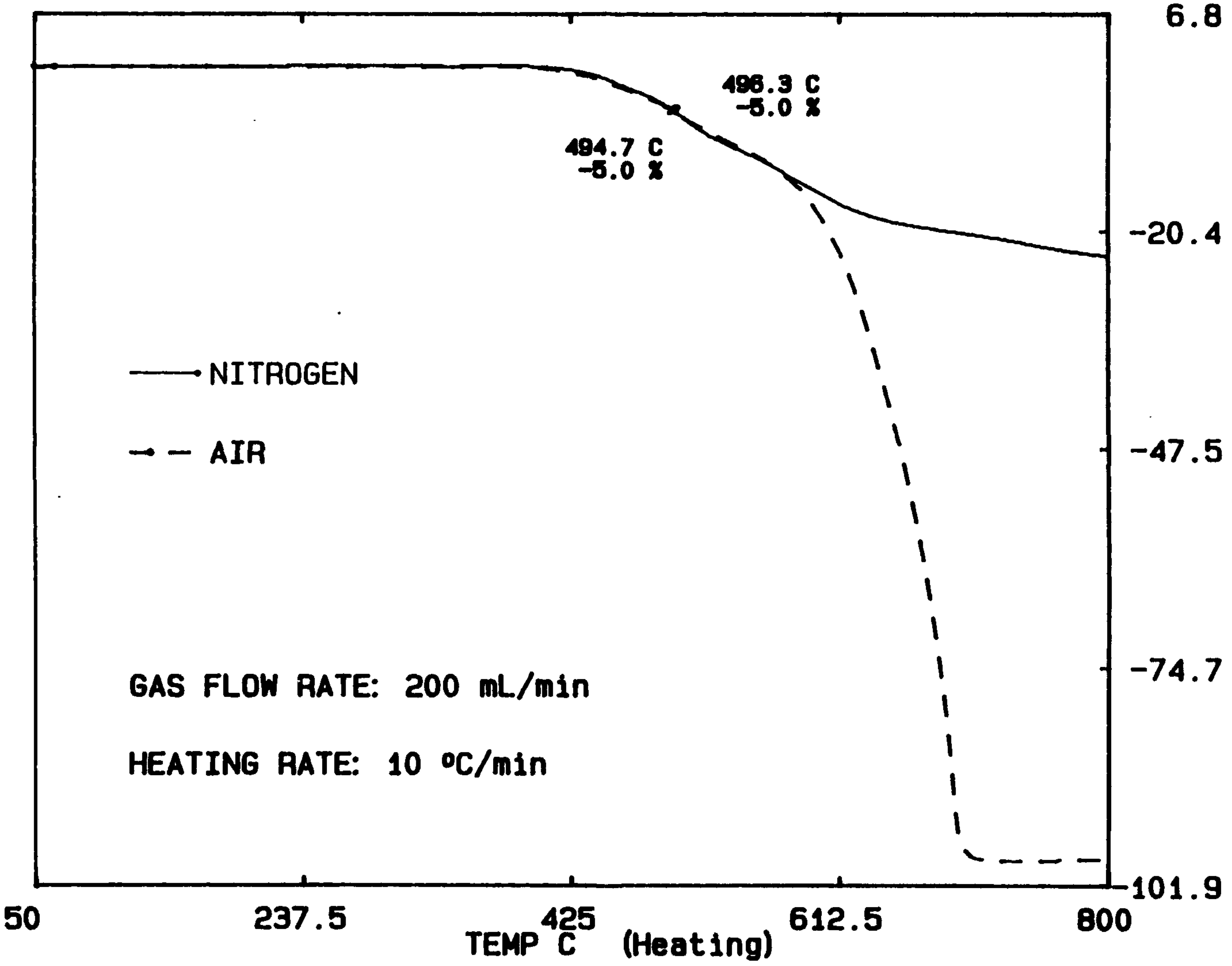

5
-23.8
-52.5
-81.3
-110
TG %
50
237.5
425
612.5
800
TEMP C (Heating)
558.5 C
-5.0 %
518.3 C
-5.0 %
NITROGEN
AIR
GAS FLOW RATE: 200 mL/min
HEATING RATE: 10 °C/min

Figure 2.



<Mn> = 12.4 x 10^3 g/mol
MWD = 1.53

Figure 3.


6.8
-20.4
-47.5
-74.7
-101.9
TG %
50
237.5
425
612.5
800
TEMP C (Heating)
496.3 C
-5.0 %
494.7 C
-5.0 %
NITROGEN
AIR
GAS FLOW RATE: 200 mL/min
HEATING RATE: 10 ºC/min