

# Synthesis of PPV-type Polyazomethine with Ordered Direction of Azomethine Linkage from AB Monomer Using Soluble Precursor Polymer Method

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## Introduction

Most polycondensations involve several monomers. Consider a system in which two bifunctional monomers are present. If the two types of reactive groups are unbalanced, the highest possible  $X_{AV}$  (the number average degree of polymerization) is finite. It is achieved when all groups of the less frequent type have reacted and the excess groups of the other type occupy all chain ends.[1] When one monomer is present in excess to the amount of 1 mol-%, then at 100 % conversion the value of  $X_{AV}$  is calculated to be 201 according to the Carothers equation. It illustrates how drastic an effect stoichiometric imbalance has on the molecular weight. When AB-type monomer bearing two functional groups with self-condensation ability is used, there is no need for the strict stoichiometric balance of monomer.

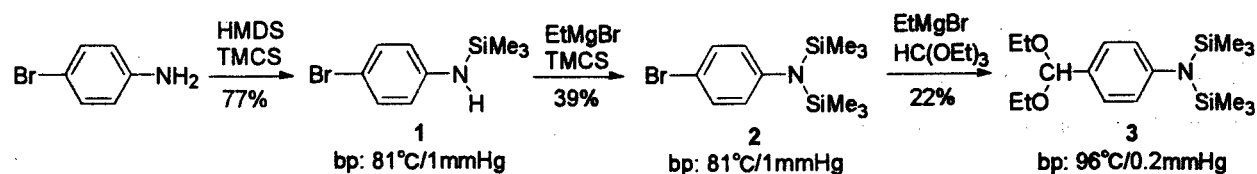
It has well-known that fully conjugated polyazomethines formed from ordinary aromatic diamines and dialdehydes are precipitated even during the initial stage of the polymerization due to their rigid-rod chain structures,[2] although they are expected to exhibit excellent properties such as thermal stability, electric conductivity, nonlinear optical properties, or many other characteristics.[3-10] The resulting precipitates are insoluble in organic solvent and do not have free-standing film formability. Therefore, these interesting properties have so far been estimated using powdery or spin-coated samples in almost all cases. Recently, much effort has been put forth on synthesizing soluble polyazomethine with film formability.[11-18] Suematsu and co-workers reported the synthesis of some film-forming aromatic polyazomethines using *m*-cresol as a polymerization medium, whereas some polyazomethines precipitated from *m*-cresol as a colored powder during the polymerization process.[19] Other methods have been also reported to improve the processability of conjugated polyazomethines by modification and selection of the polymer structure, for example, unsymmetrical[20] or symmetrical[21,22] substitutions in the main chain aromatic rings with flexible alkyl or alkoxy side chains. In 1997, we reported the synthesis, characterization, and properties of fully conjugated, soluble, and film-formable polyazomethines which were made from two types of diamines with a tetraphenylethene structure and dialdehydes.[23] Insoluble polymers having high molecular weight can be prepared using soluble precursor-polymer technique, which is well-known in poly(*p*-phenylenevinylene)[24-26] or polyimide synthesis.

In this article, we now describe the synthesis of fully conjugated and order-structured polyazomethines

from AB-type monomers using soluble precursor technique.

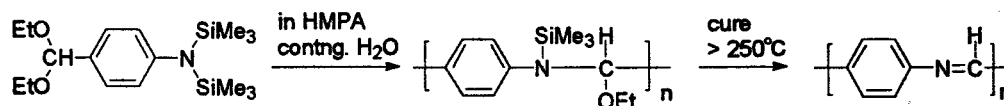
## Results and Discussion

An AB monomer, *N,N*-di(trimethylsilyl)amino-*p*-benzaldehyde diethyl acetal (**3**), studied in this work was prepared via three steps from *p*-bromoaniline as a starting material. The synthetic route is illustrated in Scheme 1 with the yields and the boiling points. The chemical structures were confirmed using IR, NMR, and elementary analyses.



Scheme 1 Synthetic route to AB monomer **3** for aromatic polyazomethine.

The PPV-type polyazomethine was synthesized using two-stage method (Scheme 2). The first stage of polymerization was carried out in HMPA containing a small amount of water at room temperature. In the preliminary MALDI-TOF mass spectrum of the precursor polymer, the peaks were observed at 2551.36, 3094.20, 3910.62, 4469.98, 5016.43, 5901.42, 7317.84, 7853.79, 9678.86, and 10959.91 *m/z* with more than 20% intensity. In an intensity range of 10-20%, we can find the peaks at 38574.03, 49845.44, and 123480.44 *m/z*. The polymerization solution was cast on a glass plate and the glass plate was heated on a preheated hot plate around 250-350 °C. After curing, the glass plate was immersed in boiling water to facilitate removal of the free-standing polyazomethine film. In the IR spectrum, strong absorptions at 1630  $\text{cm}^{-1}$  assigned to  $\nu_{\text{C}=\text{N}}$  of the aromatic azomethine group. The film was reddish brown and insoluble in common organic solvents. The further characterization of the polymer and the study of polymerization mechanism are currently underway.



Scheme 2 Polyazomethine synthesis from AB monomer using soluble precursor polymer method.

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