

In summary, 4- or 5-substituted-2-amino-3-cyanofuran was selectively synthesized and was utilized for the synthesis of pyrrolo[2,3-d]pyrimidine via guanidine cyclization reaction.

Typical Procedure:

Synthesis of 2-Amino-3-cyano-4-methylfuran 1a.

Acetol (3.7 g, 50 mmol) was dissolved in methanol (20 mL) with stirring under an atmosphere of nitrogen and a mixture of malononitrile (3.5 g, 53 mmol) and triethylamine (6.96 mL, 50 mmol) in methanol (25 mL) was added slowly dropwise at such a rate as to maintain the reaction temperature below 40 °C. After 20 min., the reaction mixture was diluted with water (50 mL) and extracted with methylene chloride (2×50 mL). The organic layers were combined, dried (Na₂SO₄) and condensed to a brown solid. Recrystallization from ethyl acetate-hexane gave **1a** (4.8 g, 39.3 mmol, 79%) as pale yellow needles: mp 155-157 °C; ¹H NMR (CDCl₃) δ 6.57 (s, 1H, =CH), 4.78-4.99 (br s, 2H, NH₂), 2.01 (s, 3H, CH₃).

Synthesis of 2,4-Diamino-5-methylpyrrolo[2,3-d]pyrimidine 4a. To a solution of guanidine free base (from 20 mmol of guanidine hydrochloride and 20 mmol of NaOMe) in anhydrous EtOH (50 mL) was added the aminonitrile **1a** (1.52 g, 10 mmol) and the mixture was refluxed for 36 h. The mixture was cooled in ice bath and the precipitated solid was filtered, washed with MeOH, and dried to give **4a** (720 mg, 4.1 mmole, 41%) as a white solid. The mother liquor was then concentrated under reduced pressure and the resulting precipitate was collected by filtration and dried to yield an additional 450 mg of pure **4a** as a white solid (overall yield 67%); mp 166-168 °C; ¹H NMR (DMSO-d₆) δ 10.49 (s, 1H, NH), 6.40 (s, 1H, =CH), 6.30 (s, 2H, NH₂), 5.40-5.75 (br s, 2H, NH₂), 2.20 (s, 3H, CH₃).

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Convenient One-Pot Synthesis of Polystyrene Copolymer Containing Thiocarbamate Group

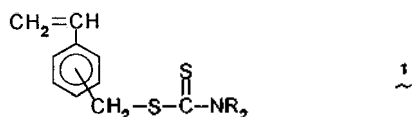
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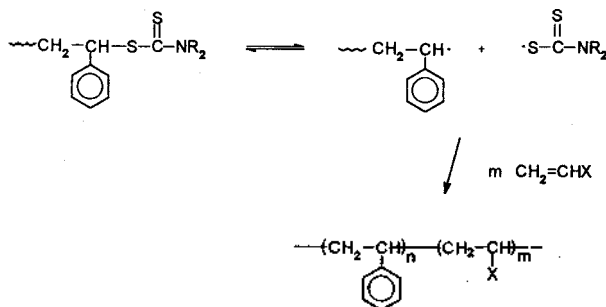
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Organic compounds containing dithiocarbamate group have been used extensively primarily for the vulcanization of rubbers. But they have received quite attention in radical polymerization because they can be applied to the synthesis of block and graft copolymers.^{1,2} For example, by thermal or by UV activation, a polymer chain having a dithiocarbamate group is dissociated and generate two radicals; one is a polymeric radical and the other is a relatively stable thiocarbamate-radical as shown in Scheme 1. Activation of the dithiocarbamate functionalized polymer in the presence of a second monomer, therefore, generates block or graft copolymers.^{2,3} During the polymerization the thiocarbamate radical caps the growing radical reversibly.

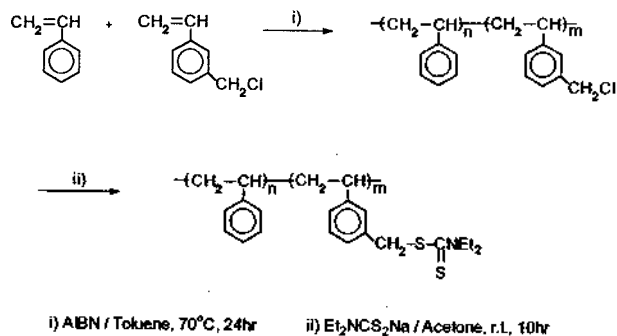
An easy preparation method of prepolymer containing dithiocarbamate group, therefore, has a significant meaning. There are a couple of ways to prepare prepolymer containing dithiocarbamate group depending on the location of the group on the polymer chain. Polymers with the pendant dithiocarbamate groups which are randomly distributed on the polymer chain have been prepared by copolymerization of a vinyl monomer containing dithiocarbamate² such as vinylbenzyl dithiocarbamate **1**.



In this report, however, a prepolymer containing dithiocarbamate was easily prepared for the first time by an one-pot synthesis as shown in Scheme 2. The second reaction step involves a polymer reaction which seems to be difficult to carry out. But this reaction led to facile conversion to the corresponding product.



Scheme 1.



Scheme 2.

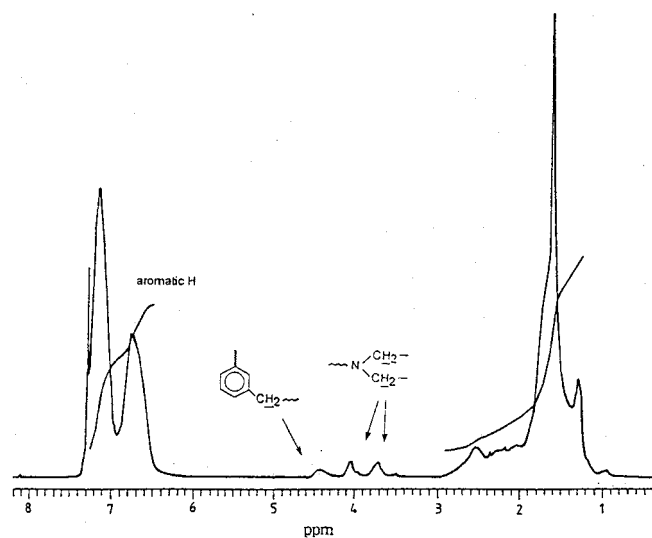


Figure 1. Proton NMR spectrum of styrene copolymer.

Copolymerization of styrene with *m*-chloromethylstyrene was carried out at first using azobisisobutyronitrile (AIBN) in toluene at 70 °C, followed by the reaction with sodium *N,N*-diethylthiocarbamate dissolved in acetone for 10 hr at room temperature.⁴ The resulting polymer was then isolated by precipitation into methanol. It was found that the chloride group was converted into the dithiocarbamate group quantitatively by proton NMR analysis. As shown in Figure 1, the chemical shifts at 4.4 and 3.9 ppm correspond to resonances of $-\text{Ph}-\text{CH}_2-$ and $-\text{S}-\text{C}(=\text{S})-\text{N}(\text{CH}_2\text{CH}_3)_2$, respectively, with integral ratio of 1 : 2. Peak splitting at about 3.9 ppm arises from hindered rotation around the C-N bond.

From the integration of the NMR peaks content of the dithiocarbamate group was determined. This determination method, on the other hand, have not been used extensively. Instead, many researchers relied on elemental sulfur analysis⁵ or UV spectroscopy.⁶ The NMR characterization method in this study was sensitive enough to determine the functionalities of polystyrene prepared by various methods. Telechelic polystyrene prepared by thermal homolysis of tetraethylthiuram disulfide showed functionality of almost 2.0 as predicted^{3,7} when the number average molecular weight was 18,100 determined by gel permeation chromatography. When polystyrene was prepared by initiation of AIBN in the presence of diethylthiuram disulfide,^{7,8} functionality was ranged from

1.0 to 2.0.

Because the second step gives quantitative conversion easily, this one-pot synthesis has a couple of advantages. Omitted preparation step of the dithiocarbamate containing monomer eliminate a rather tedious purification step,⁹ and this makes the synthesis more convenient and less time consuming. One can avoid chain transfer reactions between dithiocarbamate groups and free radical species during copolymerization. Besides, it is easy to predict copolymer composition because the reactivity ratio of chloromethyl styrene is quite well documented compared to that of 1. Because used substitution reaction condition is very mild, this synthetic scheme is applicable to many copolymer systems containing other than styrene.

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- Monomer content in feed was 46 wt% and AIBN concentration was 0.34 mol% to the monomer. Polymer yield was 64% after 24 hr. Mole fraction of comonomer in feed was 3.9 mol%, and that in polymer was 4.1 mol%. Number average molecular weight of the obtained polymer was 39,000 with polydispersity of 1.98.
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- Vinylbenzyl dithiocarbamate is purified by recrystallization from methanol with 80% yield (ref. 2). Reported mp of the para derivative is 57 °C.

Enhancement of Initiator Efficiency in Cationic Polymerization of Isobutyl Vinyl Ether

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It has been reported that an added Lewis base (or election