A New Macroazo-Initiator for the Synthesis of Polymers with Crown Ether Units

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Crown ethers which have the ability to form complexes with the cations of alkali metals and alkaline earth metals are of increasing interest.¹ The incorporation of a crown ether segment into the backbone of a polymer can induce complexing in the polymer. In order to combine crown ether structure with a polymer, most approaches have been made through the condensation reactions.²⁻⁴ In these reactions, the derivatives of crown ethers were used as two functional monomers. On the other hand, Smid and co-workers⁵ synthesized 4'-vinyl benzo crown ether, which may contribute to the formation of polymers having pendant crown ether groups.

Macroazonitriles (prepared by the use of 4,4'-azobis(4-cyanopentanoyl chloride) [eq.(2)] enables the synthesis of poly(vinyl chloride)-poly(ethylene oxide) block copolymers.⁶ Another technique⁷ has also been used for the chain extension of polymers and block copolymerization via photochemically active dibenzazepine units introduced to the polymers by means of this acid chloride [see eq.(2)].

In this article, we report the synthesis of a polyamid from *trans*-4,4'-diaminodibenzo-18-crown-6, a new macroazo-initiator having appropriate functionality for subsequent vinyl polymerization. The polyamid, is a useful initiator for free-radical polymerizations, yields polymeric products having one or two crown ether groups in accord with the normal kinetic behavior of the particular monomers involved.

EXPERIMENTAL

Synthesis of Trans-4,4'-diaminodibenzo-18-crown-6



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Trans structure of the diamine [eq.(3)] was prepared by the method of Shehori et al.⁸

Synthesis of 4,4'-azobis(4-cyanopentanoyl chloride)

The diacide chloride was prepared⁹ by reacting 4,4'-azobis(4-cyanopentanoic acid) [eq(1)] with phosphorus pentachloride in benzene. Pale yellow leaflets were obtained by precipitation in methylene chloride with the addition of hexane.

Preparation of Macroazo-Initiator

The experimental setup consisted mainly of a 100-mL three-necked flask equipped with a stirrer, nitrogen inlet, and a drying tube. 0.184 g (4.7 mmol) of trans-4,4'diaminodibenzo-18-crown-6 [eq.(3)] dissolved in 15 mL dry dimethylformamide was placed in the flask. A solution of 0.150 g (4.7 mmol) 4,4'-azobis(4-cyanopentanoyl chloride) [eq.(2)] in 15 mL dry methylene chloride was added slowly to the chilled solution. The reaction was continued overnight at room temperature under nitrogen atmosphere. Polymerization was accompanied by darkening of the solution and formation of dimethylformamide hydrochloride crystals. The polymer was precipitated by pouring the polymerization mixture into rapidly stirred crushed ice water. After it had dried, 0.126 g brownish polyamid [eq.(4)] was obtained having solution viscosity $[\eta] = 0.15$ in DMF at 25°C. Although this oligometric product started decomposing at lower temperatures, its melting point was observed to be above 350°C. As a crude demonstration, the macroazo-initiator became fibrous on heating. The infrared spectrum of eq.(4) is given in Figure 1. The polyamid structure was easily distinguished from the starting acid chloride by the strong band at 1670 cm^{-1} (CONH).



A NEW MACROAZO-INITIATOR

Polymerization Procedures

Appropriate solutions of macroazo-initiator and monomer in Pyrex vessels were degassed in the usual manner. After heating at 70°C polymers were recovered by precipitation into methanol.

Cationic Complexing of Polystyrene

This was achieved by stirring an aqueous solution of potassium picrate and the solution of polystyrene with crown ether units in benzene at room temperature. The volume of the aqueous solution was deliberately kept low so as to prevent the precipitation of the polymer while stirring.

RESULTS AND DISCUSSION



Styrene was used as a representative monomer to test the efficiency of the macroazoinitiator for free-radical polymerization. Macroazo-initiator may be decomposed on heating to give polymeric radicals [eq.(5)]. Smith⁹ postulated that the diffusion of radicals out of the solvent "cage" is effected by the rigidity of the chain. It may be assumed that intrachain species, like crown ether, prevent diffusion until combination takes place.

A typical polymerization of bulk styrene at 70°C with 50 (g/L) macroazo-initiator and a sufficient amount of DMF to facilitate dissolution produced a yield of 8.3% of polystyrene after 1 h. A control experiment without (4) produced very little polymer after the same reaction time. The infrared spectrum of the obtained polymer exhibits bands at 3400 (N—H stretching), 1650 (C=O stretching), 1600 (N—H bending), and 1130 cm⁻¹ (C—O stretching) in addition to usual the absorption bands of polystyrene.

Samples of polystyrene are obtained by initiation with (4) subjected to cationic complexing using potassium picrate. The solution of polystyrene in benzene became yellow in color as a result of complex formation of the crown ether portion of the polymer with K^+ . The UV spectrum of the solution showed absorption in the 350-nm region, indicating picrate units.

Although these results are preliminary in nature, they serve to indicate the efficiency and convenience of using macroazo-initiator to introduce crown ether units into the polymer backbone. Such processes would have considerable value in purification of liquids and in ion exchange technology. Further work is in progress to clarify procedural details and prepare the polymers by photodecomposition of the macroazo-initiator.

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