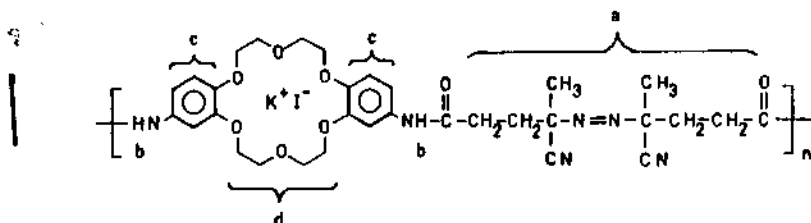


Preparation of the Macroazo-Initiator by Interfacial Polymerization

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Recently, we have synthesized¹ a macroazo-initiator (I) for the synthesis of polymers with crown ethers units by solution condensation reaction.



Conventional condensation polymerization is more sensitive to the monomer purity and stoichiometry than interfacial polymerization although it proceeds at appreciable rates. On the other hand, the complexation of the polymer supported crown ethers has great importance and it is the first fundamental process in phase transfer reactions.² In this communication, we now report the interfacial polycondensation for the synthesis of the macroazo-initiator. We further demonstrate the general value of the cationic complexing property of crown ethers placed in polymers. This method also provides complexation of the crown ether moiety before the polymer is synthesized.

The stirred interfacial polycondensation was carried out at room temperature. A two-necked flask provided with an Ultra-Turrax stirrer (20,000 rpm) and a separatory funnel was charged with aqueous solution of KI complex salt of *cis* or *trans*-4,4'-diaminodibenzo-18-crown-6 (DADC) which were prepared by Pedersen's method³ and K_2CO_3 . A methylene chloride solution of 4,4'-azo-bis(4-cyanopentanoyl chloride) (ACPC), was synthesized from the corresponding diacid⁴ and was placed in separatory funnel. The stirrer was turned on to its maximum speed and the contents of the separatory funnel were added in one portion. Stirring continued for about 8 minutes. The light brown polymer which spontaneously formed was removed by filtration. The product was washed successively with water, ethanol, and ether, and dried in a vacuum oven at room temperature. Polycondensation between *cis* and *trans* derivatives of DADC and ACPC resulted in good yields as summarized in Table I. The rather high viscosity of the *cis* product might be ascribed to better solubility of the corresponding starting diamine and higher diamine/acid chloride mol ratio. The infrared spectrum of the polyamide showed similar bands to the uncomplexed polyamide.¹ The ¹H-NMR spectrum of *cis* polyamide is shown in Figure 1. UV absorbance of ($-N=N-$) (λ_{max} 345 nm, ϵ 20.9)⁵ was hidden by the broad absorbance of diamino dibenzo-18-crown-6 (λ_{max} 338 nm, ϵ 14000).⁶

Styrene and methyl methacrylate were subjected to the KI complexed macroazo-initiator initiated polymerization. As can be seen from Table II, using *cis* macroazo-initiator yielded higher molecular weight polymers, probably due to a Trommsdorf effect since the viscosities of *cis*-initiated systems were higher than those of the *trans*-initiated systems. Composition of the obtained polymer backbone arises from