Preparation of the Macroazo-Initiator by Interfacial Polymerization

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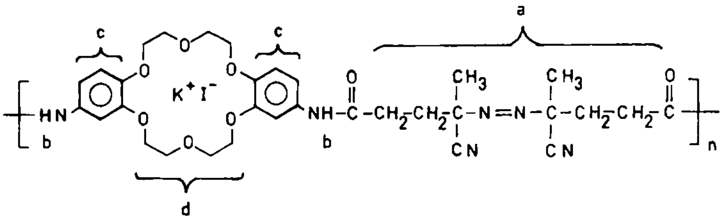
Recently, we have synthesized[1] a macroazo-initiator (I) for the synthesis of polymers with crown ethers units by solution condensation reaction.



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 method[3] and K_2CO_3. A methylene chloride solution of 4,4′-azo-bis(4-cyanopentanoyl chloride) (ACPC), was synthesized from the corresponding diacid[4] 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

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TABLE I

Stirred Interfacial Polymerization of KI Complexed Salt of DADC and ACPC at Room Temperature

	Organic Phase		Aqueous Phase			Product				
Run No.	ACPC (mg)	Methylene Chloride (ml)	KI comp. salt of DADC (mg)	K_2CO_3 (ml)	H_2O (ml)	Yield (mg)	Yield (%)	[η][a] (dL/g)	N (%)	ACPunit (mol fraction)[b]
1	158	40	400 (cis)	138	50	285	43	0.38	10.3	0.98
2	158	40	200 (Trans)	138	50	169	52	0.23	9.9	0.94

[a] 30°C in DMF.

[b] Calculation of composition based on the N content of the polyamide, N = 10.5% being 1 mol fraction of ACP unit.

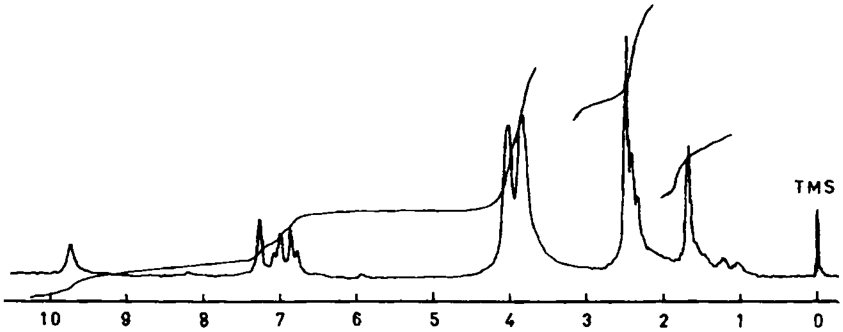

Fig. 1. ^{1}H—NMR spectrum of KI complexed cis macroazo-initiator in DMSO-d_6 + DMF d_7(1/1), 100 MHz δ = 1.2-2.7 (a, 14H), 9.7 (b, 2H), 6.5-7 5 (c, 6H), 3.9 (d, 16H).

TABLE II
Polymerization of Styrene and MMA in DMF Initiated by KI Complexed Macroazo-initiator at 70°C

Monomer (M)	KI Complexed Macroazo-initiator (g/L)	Reaction Time (Min)	Conversion (%)	[η]^a (dL/g)
St (6.43)	Cis (3.70)	120	7	1.11
St (6.43)	Trans (3.70)	120	8	0.46
St (4.34)	Cis (5.00)	120	8	0.78
St (4.34)	Trans (5.00)	120	9	0.26
St (4.34)	Cis (12.50)	120	12	0.38
St (4.34)	Trans (12.50)	120	13	0.36
MMA (4.70)	Cis (12.50)	120	37	0.54
MMA (4.70)	Trans (12.50)	120	44	0.37

^{a}30°C in DMF.

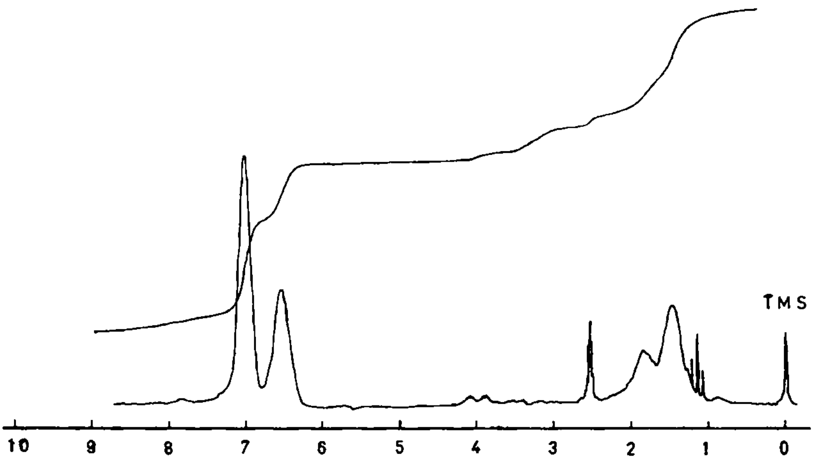

Fig. 2. ^{1}H—NMR spectrum of polystyrene obtained with KI complexed cis-macroazoinitiator in DMSO-d_6 + DMF-d_7 (1/1), 100 MHz, δ = 6.5-7.5 (Ar-H), 4.0 (aliph.-H in Crown ether), 2.45 (aliph,-H in ACP), 1.0-2.0 (aliph.-H in St).

TABLE III
The K Contents[a] of The Products at Various Stages

Product	Calculated K (%)	Found K (%)
KI Complexed Salt of Trans-4,4′-diaminodibenzo-18-crown-6	7.01	6.93
KI Complexed Macroazo-initiator	4.87[b]	2.22
Polystyrene	—	0.35

[a] Measured by flame photometry (Eppendorf).

[b] End groups are neglected.

both specific mechanism of termination and the number of —N=N— linkages in the main chain of the initiator. Crown units are expected to be part of the block copolymer. However, the segment length of the polyamide is small, because further decomposition in block copolymer occurs through azo linkages present in the backbone. This consideration would be supported by ^{1}H—NMR spectrum of the obtained polystyrene (Fig. 2). Inspection of the intensity of signals suggested that each block copolymer chain contains approximately 70 styrene units per crown ether unit.

Further, potassium contents of the related reaction products at various stages are given in Table III. The low potassium content of the macroazo-initiator may be attributed to the tendency of the complexed crown ether to release its salt to the aqueous solution. Pedersen claimed[3] that most of the complexes were dissociated in water and temperature.

Detailed studies of the preparation of the macroazo-initiator having a desired small number of —N=N— linkages in the main chain and description of block copolymerization starting with crown ether and azo containing polyamides are now in progress.

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