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Novel Electron Transfer Polymerization Processes with Alkali Metal Supramolecular Complex as Catalyst

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SUMMARY: Single electron transfer SET induced usually by organometallic complexes of transition metals or alkali metal complexes of arenes e.g. naphthalene is common in organic reactions. In this paper unusual two-electron transfer to suitable acceptor molecule mediated by recently discovered alkali metal supramolecular complexes in aprotic etheral solvents is presented. The capability of these solutions of transferring two electrons to a suitable organic substrate and formation of corresponding carbanions opens new door in synthetic chemistry. The carbanions are interesting synthons in the many organic reactions and catalysts in anionic polymerization processes. Reactions of some vinyl compounds, alkyl and silyl halides, as well as ring-opening polymerization of β-lactones and oxiranes are discussed.

Introduction

Electron transfer is very common in chemistry playing also an important role in polymerization processes. The single electron transfer mechanism SET is usually induced by organometallic complexes of transition metals(1), photo- or radiation induction(2) and alkali metal complexes of arenes e.g. naphthalene(3). These electron donors are capable of transferring one electron to a monomer, usually to vinyl or acryl compounds as well as to olefines or dienes. Due to electron transfer radical-anions are formed as the first intermediates in such SET polymerization reactions.

Discovery of macrocyclic and macrobicyclic complexants for alkali metal cations by Pedersen(4) and Lehn(5) enabled dissolution of alkali metals in aprotic organic solvents. The resultant so called "alkali metal organic blue solutions" containing complexed metal cations, metal anions and solvated electrons(6) were used as initiators in various polymerization processes(7). However, the reaction mechanisms were not clear because the compositions of

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such solutions and ratios of electrons and metal anions were not well defined. The studies on kinetics of metal dissolution enabled the rationalization of the metal dissolution process and the preparation of metal solutions containing only alkali metal ion pairs, e.g. K^+/Ligand, K^- (Ligand = crown ether or cryptand) was possible[8]. The concentration of metal ions in such solutions is equal to the concentration of added ligand (usually 0.1-0.5 mol/L), the concentration of electrons being as low as 10^{-4} mol/L.

It turned out that alkali metal supramolecular complexes are active as initiators capable of transferring two electrons to a monomer to produce corresponding carbanions[9] (Scheme 1).

$$2M + L \longrightarrow M^{\oplus}L + M^{\ominus}$$

$$M^{\ominus} \xrightarrow[\text{transfer of } 2e^{\ominus}]{\text{substrate}} M^{\oplus} + \text{carbanion}$$

Scheme 1

The two-electron transfer is very unique in synthetic chemistry, and has been utilized by us in vinyl-, ring-opening and in reductive coupling polymerization. Supramolecular complex of potassium K^+/18-crown-6, K^- has been employed as initiator in these reactions.

The direct evidence of carbanion formation as an intermediate in the initiation of polymerization has been provided by ^{39}K NMR technique. The Fig. 1a shows the fingerprint of K^+/18-crown-6, K^- solution in THF and Fig. 1b this solution after the reaction with a suitable electron acceptor. The signal of K^- disappears after two-electron transfer and the intensity of the signal of potassium cation is increased.

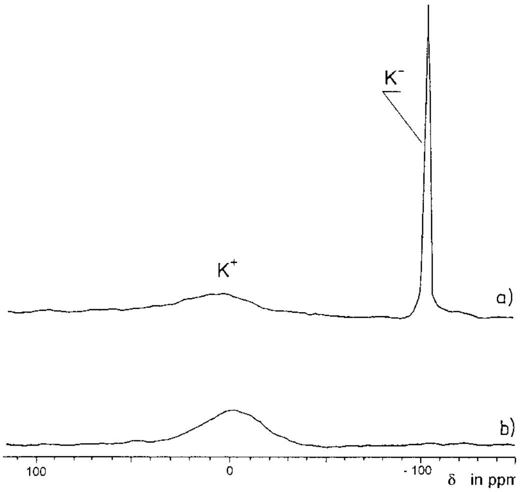
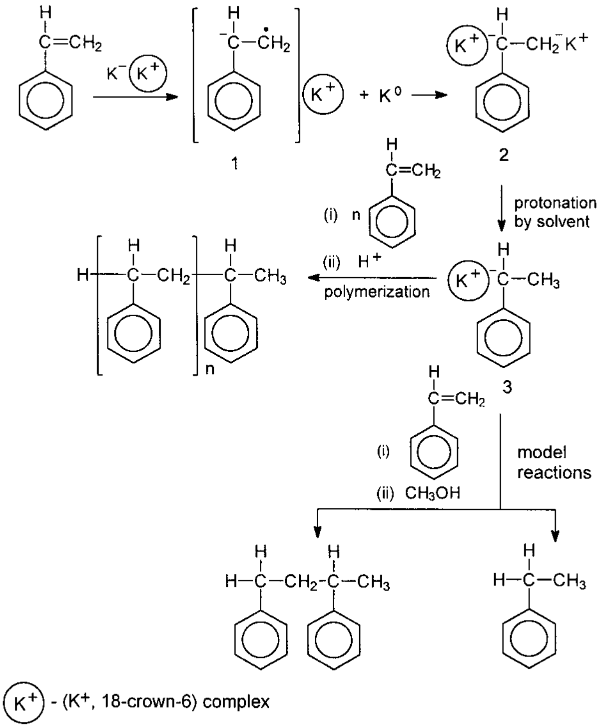


Figure 1. a) ^{39}K NMR of the potassium ion pair with 18-crown-6 in THF solution before a reaction; b) ^{39}K NMR of this solution (a) after a reaction

Some novel polymerization reactions are described in next sections.

Polymerization of vinyl monomers

Polymerization of styrene with sodium naphthalenide as initiator is known for many years[3,10]. In this reaction the transfer of one electron yields a radical anion as an initial product. The recombination of two radical anions gives a dimeric dianion. If a supramolecular complex of potassium is used as the electron donor the reaction proceeds differently and the direct formation of a unique styrene dianion is observed[11]. Similar unusual two-electron transfer to α-methylstyrene has also been demonstrated. The transfer of two electrons to styrene or α-methylstyrene, respectively, occurs and the styrene carbanions formed are capable of transferring their charge to neutral molecules, thus inducing various reactions as well as polymerization processes (Scheme 2).



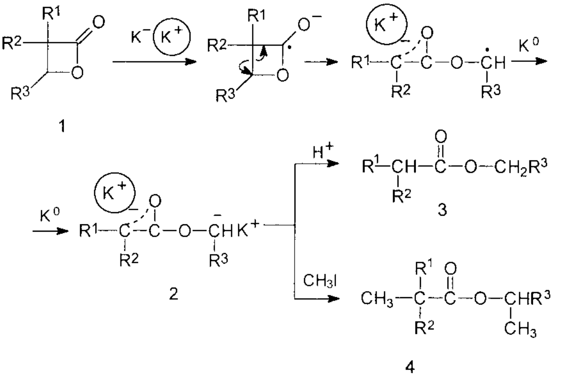
Scheme 2

Using this method, facile synthesis of styrene - ester block copolymers can be accomplished. Thus co-polymerization of styrene with lactones can be used as convenient method of amphiphilic polymer synthesis.

Methylmethacrylate polymerization with a supramolecular alkali metal ion pair proceeds similarly as that of styrene. Due to two-electron transfer from the ion pair to the monomer methylmethacrylate carbanion is formed able to induce living polymerization of the monomer[12)].

Ring-Opening Polymerization of β-Lactones

It is well known that hydrolysis, alcoholysis and acidolysis of four-membered β-lactone rings proceed via alkyl-oxygen or acyl-oxygen bond cleavage. However, an unusual C-C bond scission in the strained β-lactone ring by the potassium metal supramolecular complex K^+/18C6, K^- in THF solution leading to enolate carbanion 2 formation has been observed due to two electron transfer from the metal anion outer orbital[13)] (Scheme 3).

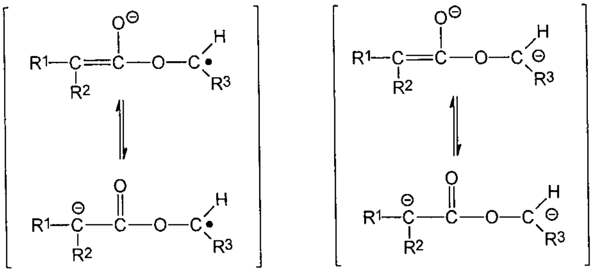


1,2,3,4	R^1	R^2	R^3
a	H	H	H
b	CH_3	C_2H_5	H
c	H	H	CH_3

(K^+) - (K^+,18-crown-6) complex

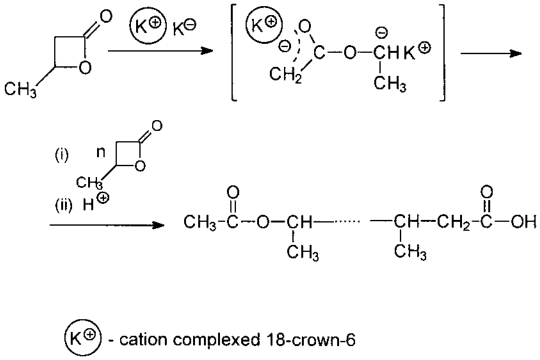
Scheme 3

The evidence for the two-electron transfer from the metal anion to a lactone was provided also by ^{39}K NMR of the metal solution before and after the reaction (Fig. 1). The driving force of this unique C-C bond cleavage in β-lactones is obviously the strong resonance stabilization of the intermediate enolate radical and carbanion (Scheme 4).



Scheme 4

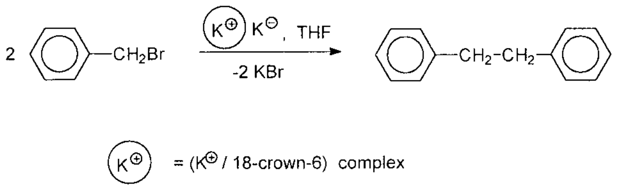
The intermediate carbanions can serve as a useful synthons in various reactions, such as protonation, alkylation, acylation. Such a course of these reactions is valid for unsubstituted and substituted β-lactones. If β-butyrolactone is used in excess as a monomer the reaction of β-butyrolactone with the potassium supramolecular complex yields biomimetic poly-3-hydroxybutyrate – similar to natural PHB polymer produced by enzymes in prokaryotic and eukaryotic living cells (Scheme 5).



Scheme 5

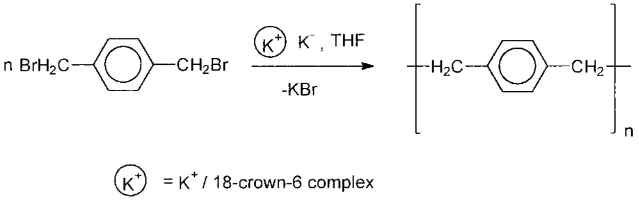
Reductive Coupling of Alkyl and Silyl Halides

The coupling of benzyl bromide proceeds smoothly at the temperature of 20°C (or lower) in the THF solution of K^+/18-crown-6, K^-. The main product of the model reaction of benzyl bromide (equimolar ratio of halide and metal ion pair) is 1,2-diphenylethane (yield 80%) (Scheme 6).



Scheme 6

If the difunctional α,α'-dibromo-p-xylene was used in the reaction with potassium supramolecular complex, unusual poly-coupling occurs, yielding poly(*p*-xylylene) (Scheme 7) with almost 100 % conversion of the monomer. The low-molecular fraction of the polymer (30%) obtained was soluble in THF, showing broad molecular weight distribution ($M_n \approx 2000$, $M_w/M_n = 2.9$)[14].



Scheme 7

The THF-insoluble high polymer is thermally stable, showing a glass transition temperature $T_g = 27°C$ and the beginning of decomposition at 265°C. The novel polyreaction of α,α'-dibromo-*p*-xylene mediated by alkali metal complexes enables the unprecedented low-temperature synthesis of poly(*p*-xylylene), previously synthesized from p-xylene or cyclophane by high-temperature thermolysis[15], or from the derivatives of benzylammonium iodides *via* elimination reactions[16]. The novel method presented in this paper is advantageous if compared with those described previously. The yield of high molecular weight fraction is around 70 %, the polymer being characterized by ^{13}C solid-state NMR (Fig. 2). The ^{13}C NMR spectrum (Fig. 2) exhibits lines at 139.6 and 129.4ppm, which are assigned to the nonprotonated and protonated aromatic carbons, respectively, whereas the methylene carbons give rise to the line at 39.4 ppm. Such assignment is consistent with that reported by Loy *et al.*[17] for the poly(xylylenes) obtained *via* thermolysis of [2,2] paracyclophane at 650°C under reduced pressure. The two remaining lines (31.4 and 18.9ppm) may be ascribed to ethyl terminal groups.

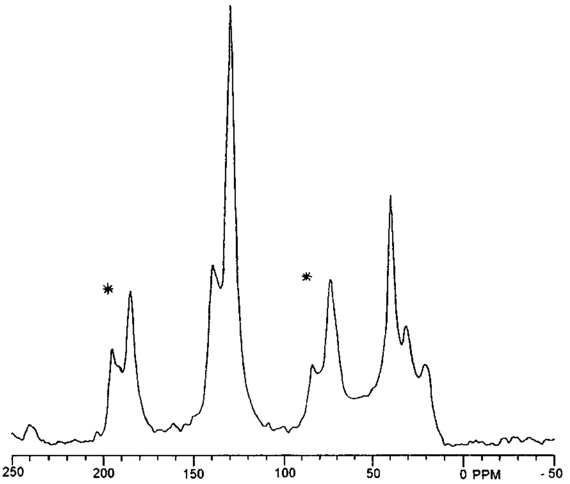
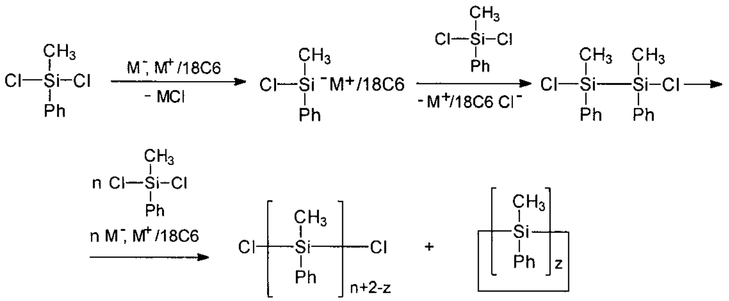


Fig. 2 75 MHz ^{13}C CP/MAS NMR spectrum of poly(*p*-xylylene); the spinning side bands are denoted with asterisks

It can be assumed that an electron transfer mechanism to benzyl bromide is operating in the reactions of the metal complex with benzyl bromide as well as in the polymerization of α,α'-dibromo-*p*-xylene.

Similar coupling proceeds in the reaction of silyl halides. Spectacular example of such reaction is provided by coupling of methylphenyldichlorosilane, which yields linear polysilanes and cyclic silane oligomers (Scheme 8)$^{18)}$. The electron transfer mechanism is operating in these reactions with formation of silicon anions as intermediates. The novel facile method of synthesis of macrocyclic polysilanes as well as linear polymers is of interest for practical applications e.g. producing materials for electronics.



where M = K or Na
z = 5,6

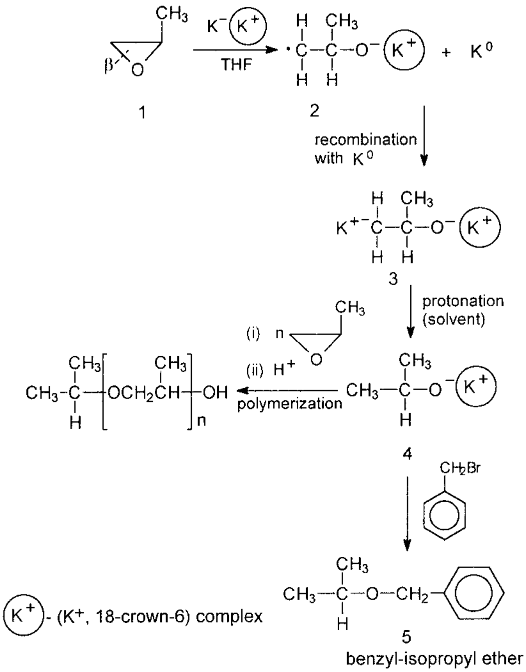
Scheme 8

Regioselective ring cleavage in epoxides

The reductive cleavage of epoxides to alcohols is a very common reaction of general use in many organic syntheses[19]. Epoxides show versatile reactivity, being able to react with nucleophiles as well as with electrophiles. The nucleophilic substitution of unsymmetrical alkyl-subsituted epoxides occurs usually *via* C-O bond cleavage at the less substituted carbon atom. However, an aromatic substituent, e.g. phenyl, may induce the ring-opening also at the substituted carbon[20].

The regioselectivity of ring-opening epoxides reaction has been studied also with various electron transfer reagents as sodium naphthalenide[21], alkali metals in liquid ammonia or in amines[22]. The theoretical rationale for the electron transfer reactions mediated by lithium naphthalenide has recently been provided by semi-empirical and thermochemical molecular calculations for ethylene oxide and some substituted epoxides[20]. We report now on the unusual two-electron transfer to epoxides mediated with alkali metal supramolecular complexes.

According to the result of the protonation or the benzylation of reaction products the following course of this reaction can be proposed (Scheme 9):



Scheme 9

In the reaction of the supramolecular metal complex (SMC) with propylene oxide one electron from a metal complex is transferred to the propylene oxide molecule, inducing oxygen-methylene carbon β-bond cleavage, and formation of radical-anion 2. Next, the recombination of this radical anion 2 with K^0 yields carbanion of an alcoholate 3. Due to instant protonation by THF solvent an alcoholate 4 is formed respectively.

If propylene oxide is present in excess, in the reaction medium poly(propyleneoxide) possessing hydroxyl and isopropyl end groups, is formed as confirmed by ^{1}H NMR (Fig. 3).

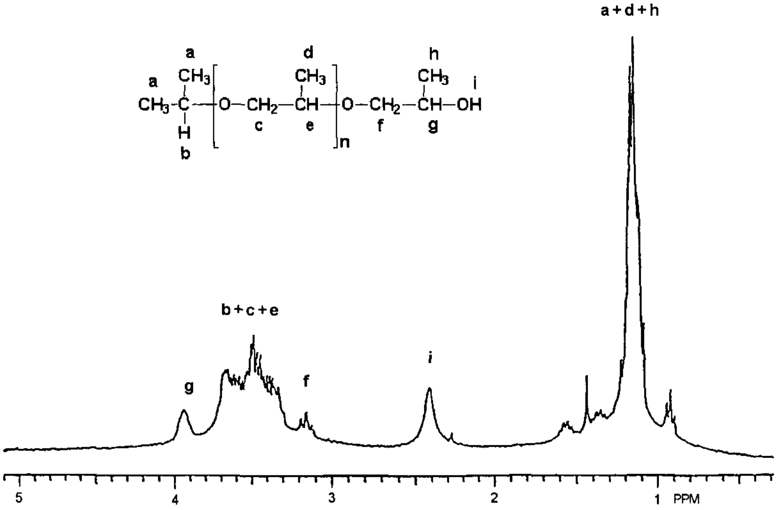
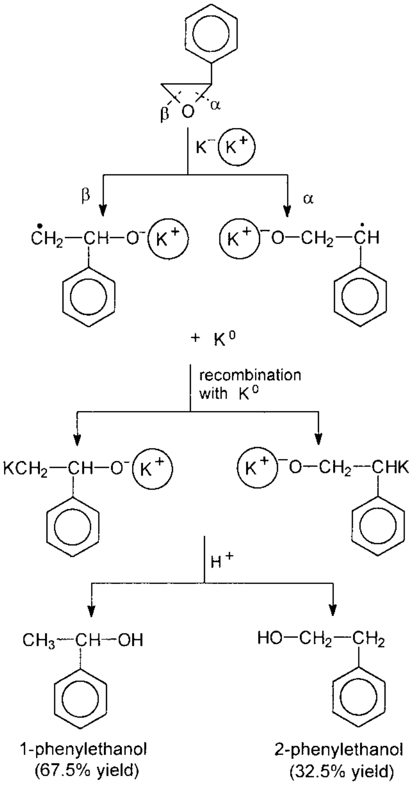


Fig. 3. ^{1}H NMR spectrum of propylene oxide polymer obtained *via* electron transfer

The reaction proceeds regioselectively. The transfer of electron proceeds towards less substituted carbon atom of propylene oxide with formation of carbinol due to C-O bond cleavage at the less substituted carbon atom (Scheme 9).

However, in the case of an epoxide, bearing aromatic substituent, e.g. styrene oxide, both β- and α-bond scission was observed (Scheme 10). It means that the inductive effect of substituent at the oxirane ring is essential.

Presented here, electron transfer to epoxides induced by supramolecular complex of potassium or sodium-potassium alloy offers new opportunities in synthesis o various derivatives of oxiranes. The presented strategy enables facile synthesis of poly(propyleneoxide) which does not contain traces of initiator. Moreover due to "living" type of this polymerization, a great variety of block polymers can be produced.



Scheme 10

The presented here methods of syntheses *via* C-C, Si-Si, C-Si bond formation as well as C-C or C-O bond cleavage in ring opening reactions proceeding *via* unprecedented electron transfer mechanisms provide novel opportunities in organic and polymer synthesis. Supramolecular approach with use of supramolecular alkali metal complex as unique two-electron transfer agent opens new door in synthetic chemistry. Novel polymer materials with well-defined tailored molecular architecture can be produced.

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