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The participation of crown ethers in the initiation of group-transfer polymerisation

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Summary

The use of crown ethers in conjunction with alkali metal salts, as catalysts in group-transfer polymerization, is discussed.

Introduction

The novel polymerisation process which was named Group-Transfer Polymerisation(GTP) by its originators[1] has a number of features which suggest a parallel relationship, in at least some respects, to Michael addition. In the case of GTP, it is clear that an anion plays a very important part in the mechanism as a catalyst acting in conjunction with the initiator, the latter being typically a silyl ketene acetal. The recommended catalysts include fluorides, bifluorides, azides and cyanides, and the example most often quoted (and therefore presumably one of the best) is tris(dimethylamino)sulfonium bifluoride ($TASHF_2$).

It is known from general chemistry that the bifluoride ion is a potent nucleophile when it is unencumbered by a closely-associated cation, so, when one tries to account for the special effectiveness of $TASHF_2$, it seems reasonable to suppose that the great bulk of the heavily substituted sulfonium cation results in a large separation of positive and negative centres. The consequent weakening of the inter-ionic electrostatic forces leaves the fluoride ion essentially free. If this hypothesis is correct, other exceptionally large cationic counter-ions, or any other circumstances that render the anion free, should be conducive to efficient polymerisation.

We have tested the hypothesis by comparing the efficiencies of reactions catalysed by simple salts, specifically potassium fluoride and potassium acetate, with and without the addition of a crown ether known to complex the cation.

Experimental

Tetrahydrofuran (THF) was stored overnight over $FeSO_4$, distilled, stored over KOH, distilled, and finally redistilled from sodium benzophenone ketyl immediately before use.

Acetonitrile was shaken with molecular sieves (4A) overnight, stirred with CaH_2 until no further hydrogen was evolved, and distilled from CaH_2 just before use.

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Methyl methacrylate was purified by washing with 10% aqueous NaOH at least twice. It was dried over $MgSO_4$ for 24 hours, and stored over CaH_2 at -20°C. It was distilled immediately before use.

(1-methoxy-2 methyl-1-propenyloxy)trimethylsilane (MTS) was prepared according to the literature.[2]

Potassium fluoride and potassium acetate were each dried at 120°C for 5 hours.

All polymerisations were carried out at 50°C.

Results and Discussion

i) Potassium fluoride as catalyst.

Without a crown ether present, no polymerisation was observed on being left to react overnight. In the presence of 18-crown-6 ether, a conversion of 17% was found in otherwise identical conditions, and in the presence of dibenzo-18-crown-6 ether, the conversion was also 17%. In both cases, GPC examination demonstrated that the product has a broad molecular weight distribution, with $M_w/M_n = 6.3$ in the former case. The molecular weights were always far below those expected on the basis of the known proportions of reactants, so one must suppose that some side-reactions are occurring.

ii) Potassium acetate as catalyst.

Knowing that "naked" acetate is a very efficient nucleophile, we prepared another catalyst system by dissolving dry potassium acetate in acetonitrile containing 18-crown-6 ether. Again, although no polymer was formed in the absence of the crown ether, when it was present, a yield of 92% was obtained. Moreover, the molecular weight is close to the expected value and the molecular weight distribution is relatively narrow, with $M_w/M_n = 1.9$.

iii) Conclusions

It seems likely that any method of reducing the interaction between the cation and anion of the catalyst, including complexing the cationic component, leaves the anion free to exert strong activity in the initiation of group transfer polymerisation.

References

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