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Initiation of Cationic Vinyl Ether Polymerization by Trityl Ion Salts

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Summary

The cationic polymerization of isobutyl vinyl ether in liquid sulfur dioxide at several temperatures was initiated by the trityl halides, Ph_3C-Cl and Ph_3C-Br.
The low molecular weight products obtained were investigated by reverse phase chromatography. RPC diagrams indicate that every chain carries trityl groups. These results are considered to be proof positive for initiation by direct trityl addition to monomer in cationic vinyl ether polymerization.

Introduction

Stable trityl ion salts are suitable initiators of cationic polymerizations of many reactive monomers, however, the direct addition of carbenium ions to monomers during initiation has been proven only for tropylium ion/N-vinyl carbazole [1] and trityl ions/vinyl ethers [2, 3, 4]. The direct addition of trityl carbenium ions to N-vinyl carbazole was considered to be unlikely because of steric reasons [5].

The conclusions drawn in these papers were mainly based upon product characterization by spectroscopic methods. Taking into consideration the analysis of the gross product it could not be excluded that the polymers under investigation still contain small amounts of unreacted trityl compounds not attached to polymer chains.

The aim of this paper is it to prove that initiation in cationic vinyl ether polymerization occurs by direct addition of trityl ions to the monomer.
Accurate HPLC analyses are used to exclude artifacte by left over trityl compounds included in the polymer, without being attached to polymer chains.

Experimental

Trityl halides were prepared by the reaction of trityl alcohol with acid halides according to Organic Synthesis [6].

The products were purified by recrystallzing twice from dry heptane (CaH_2) in the presence of a few drops of the acid halide.

Sulfur dioxide was purified and dried by passing it through several colums filled with H_2SO_4, P_2O_5 and molecular sieves (Wolfen Zeosorb 3 Å) and then condensed into gratuated storage vessels. The conductivity of the SO_2 treated this way was $2.6.10^{-7}$s.
Investigations on the conductivity of trityl halides in SO_2 solutions showed that the conductivity does not change over a period of several days.

Commercially available isobutyl vinyl ether was washed twice with 5 % aquous NaOH and refluxed for several hours over CaH_2 under dry argon. Subsequently it was fractionally distilled (b.p. = 83 °C) and immediately used.

Polymerizations were carried out under dry argon in baked out jacketed glass reactors cooled by a cryostate. A well defined amount of the trityl halide was first charged in the reactor. Then the sulfur dioxide solvent was condensed into it. About 10 vol % CH_2Cl_2 were added to assure homogenous polymerization conditions. The monomer was added through a silicon rubber septum by a baked out syringe. Polymerizations were terminated by addition of a few ml of a methanol/ NH_3 mixture after four hours when the conversion was about 100 %. After evaporation of the solvent the liquid products were washed with aqueous ammonia and bidistilled water twice each. HPCL investigations were carried out with a KNAUER instrument. For GPC analysis, i.e. estimation of the molecular weight distributions, a set six colums filled with LiChrospher materials (MERCK) was used. Reverse phase chromatography (RPC) was applied to separate the product fractions according to their degree of polymerization. For this purpose a LiChrosorp RP 18 (10) colum (MERCK) was used. The flow rate was 1 ml/min at room temperature. Eluent was a mixture of methanol and chloroform (9:1). By the use of a differential refractometer and a UV photometer (254 nm) as detectors both the total distribution of the product fractions and the distribution of UV chromophores among the product fractions could be analyzed.

Results and Discussion

FIGURE 1 shows the RPC-elution diagram of a representative sample of cationically polymerized isobutyl vinyl ether (IBVE). Because of its low average molecular weight (350 by VPO) the polymer was completely soluble in methanol/chloroform (9:1) which is a suitable eluent for RPC investigations. The RPC method is axcellent for the separation of oligomer fractions according to their degree of polymerization. Because Poly(IBVE) is UV inactive at 254 nm the UV detector response reflects the distribution of chromophores (trityl groups) in the product fractions, i.e. indicates the presence of trityl groups attached to polymer chains.

In FIGURE 1 the first peak of high intensity refers to a supterposition of monomer, dimer and unreacted trityl compound which could not be separated. The assignment of these species was achieved by RPC analysis of the individual compounds. The second peak refers to the trimer of IBVE carrying one trityl group, the third peak refers to the tetramer and so on. The comparison of RI and UV detector resposes clearly shows that all product fractions contain UV chromophores, i.e. trityl groups. In other words, the cationic polymerization of IBVE in dry SO_2 was initiated by direct addition of trityl carbenium ions to the monomer followed by fast propagation. SUBIRA et al. [7] determined k_i, k_p, $k_{Tr,m}$ and k_t for the cationic polymerization of various vinyl ethers initiated by Ph_3CSbCl_6. For IBVE the rate constants follow the order:

$$k_p \gg k_{Tr,m} > k_i > k_t$$

Thus, initiation is the rate determining step. Parts of the chains, however, may also be started by proton transfer to monomer. The quantitative evaluation of the RPC diagrams is rendered very difficult. From investigations on the temperature dependence of the polymerization process, however, it can be concluded that the intensity ratio of UV and RI detector responses does not change significantly as a function of temperature.

Therefore, the fraction of chains started by direct trityl addition compared with those started by proton transfer appears to be temperature independent. Furthermore, there seems to be no variation of average molecular weight as it can be concluded from RPC, GPC and VPO measurements. This ovservation is in agreement with the results reported by SUBIRA et al. [7] on the initiation by trityl ions with complex counterions. Obviously, the polymerization of vinyl ethers initiated by trityl ion salts both with complex counterions and simple halide anions follows the same mechanism. The very low molecular weights reported in this paper (ca. 350 by VPO) as compared with the data by KUNITAKE [4] for trityl salts with complex anions (ca. 500 - 2500), hint at a fast termination by recombination of the propagating carbenium ions with the halide counterion.

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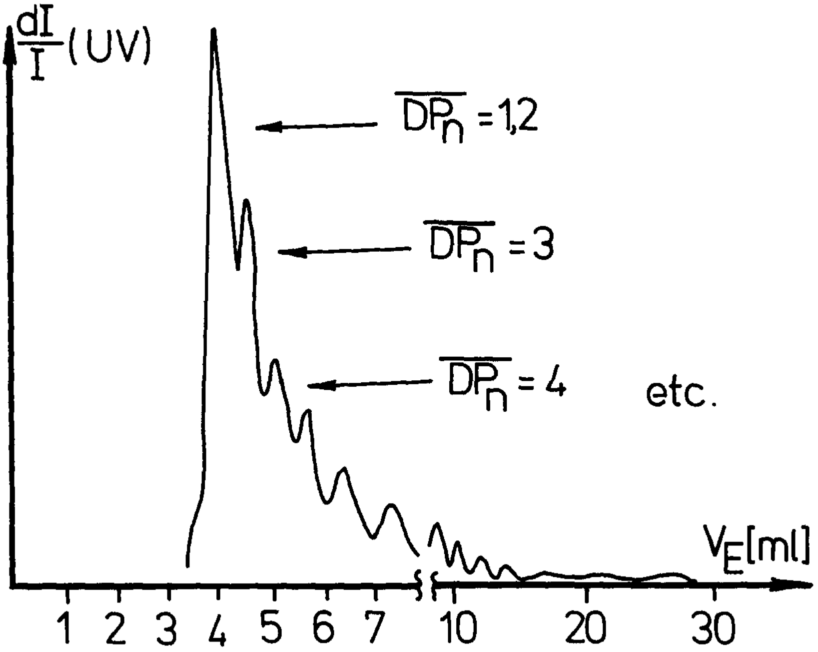

FIGURE 1: RPC-elution diagram of a low molecular weight poly isobutyl vinyl ether (initiation by Ph_3CBr)

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