Polymer Bulletin 12, 427–431 (1984)

Polymer Bulletin

Activated Aromatic Diazonium Ions, Sulfonates and Halides as New Initiators for the Cationic Polymerization of p-Methoxystyrene: Exceptional Effectiveness of p-Nitrobenzenediazonium Tetrafluoroborate

H. K. Hall, Jr. and Michael A. Howey

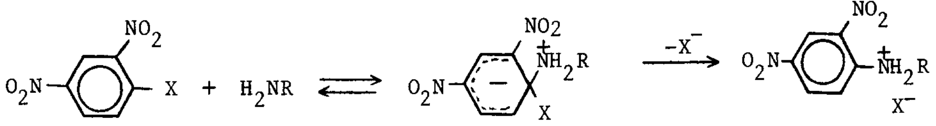
Chemistry Department, College of Arts and Sciences, University of Arizona, Tucson,
Arizona 85721, USA

Summary

Nitro-substituted aromatic diazonium ions, sulfonates, and halides initiated cationic polymerization of p-methoxystyrene in nitromethane solution. p-Nitrobenzenediazonium tetrafluoroborate was by far the most effective of five such compounds tested. The mechanism is believed to involve addition of the nucleophilic monomer to the aromatic ring to form a Meisenheimer intermediate. Elimination of the leaving group forms a carbenium ion which initiates polymerization.

Introduction

"Activated" aromatic halides are well known to react with nucleophiles such as amines and alkoxides. The reactions occur by addition of the nucleophile to the ring to form the Meisenheimer intermediate, followed by loss of the leaving group:



We can now report that 1-substituted nitroarenes can be used as effective initiators for cationic polymerization of nucleophilic monomers.

Experimental

Monomer: p-Methoxystyrene (Aldrich) was distilled from calcium hydride.

Solvent: Nitromethane was purified by literature procedure (Parrett and Sunn, 1977).

Initiators: 1-Fluoro- **1** and 1-chloro-2,4-dinitrobenzene **2** are commercially available. The other derivatives were prepared according to literature procedures: 2,4-dinitrobenzene-1-p-toluenesulfonate **3** (Bunnett and Bassett, 1959), 2,4-dinitrobenzene-1-trifluoromethanesulfonate **4** (Chapman and Freedman, 1971) and p-nitrobenzenediazonium tetrafluoroborate **5** (Zollinger, 1976). The latter can also be obtained commercially and was purified by precipitation of an acetonitrile solution in dry ether (m.p. 154°, lit. 156°).

Polymerization procedure: Reactants were combined in a glove bag under argon gas. The polymerizing mixtures were stirred and light was excluded. The polymers were precipitated in methanol and dried. Molecular weights were calculated from size exclusion chromatography using polystyrene standards.

Results

p-Methoxystyrene was polymerized with these different potential intiators and the results are summarized in Table I.

TABLE I

Polymerization of p-Methoxystyrene in Nitromethane

Initiator^{a,b}		Mole % Initiator	Time (h)	Temp. °C	% Yield	$\overline{M}_w$(GPC)	f^{c}
Blank		-	24	101	2	7,000	-
F	1	10	24	101	1	10,000	-
Cl	2	3	24	101	30	16,000	0.08
OTos	3	5	24	101	44	22,000	0.05
OTrfl	4	5	2	101	56	82,000	0.02
$\overset{+}{N_2}B\overset{-}{F_4}$	5	5	0	28	100	644,000	0.004^{d}
$\overset{+}{N_2}B\overset{-}{F_4}$	5	0.01	0	28	100	1,700,000	0.79

a) Initiator 1-substituent, b) Monomer concentration = 1.25 - 2.5 mole/l.
c) f = initiator efficiency, d) Exothermic, uncontrollable.

With 1-fluoro-2,4-dinitrobenzene 1 only a 1% yield of polymer was obtained, which is the same as the blank run. When the chloro (Compound **2**) and the tosylate derivative (Compound **3**) were used, reasonable yields of polymer with moderate molecular weight were obtained. No polymer was produced in bulk reactions using these compounds as initiators.

Compound **4**, the triflate derivative, was a significantly better initiator than compounds 1-3 (50% conversion in 2 hours). The molecular weight of the polymer was 82,000. This compound gave high yield of polymer even in bulk conditions.[1] Gel permeation chromatography was used to follow the polymerization; near quantitative conversion to polymer was obtained in approximately 6 hours at 101°C with excellent reproducibility.

---

[1] Using 5 mole % initiator **4**, 15 hours, 110°C, resulted in 81% yield of polymer.

Compound 5, p-nitrobenzenediazonium tetrafluoroborate, was an outstandingly effective initiator for p-methoxysystrene. In nitromethane solution or in bulk at room temperature, there was an immediate quantitative conversion of monomer to polymer, even at initiator concentration of 0.01 mole %. The molecular weight of this polymer was 1,700,000. The reactions in bulk were so exothermic that they could not be controlled.

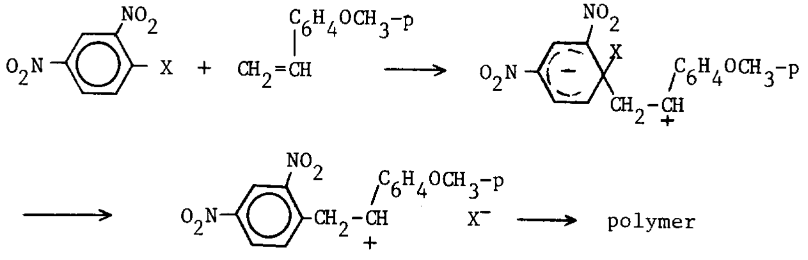
The initiator efficiencies are shown in Table I. The method of calculation is based on the assumption that no chain transfer occurs. When 0.01 mole % of the diazonium salt 5 is used as initiator, 79% of the initiator is utilized to initiate a polymer chain. In all other cases, the efficiencies are low.

A reaction with 10 mole % 2,4-dinitrophenol, a possible hydrolysis product, as initiator carried out for 19 hours at 101°, gave only a 7% yield of polymer, too small to be significant. Moreover, in an experiment using the triflate derivative 4 in sufficient concentration to raise the pH of water to 1.5 (10 mg/ml), it required 3.5 hours of boiling to do so. This excludes the possibility of hydrolysis to trifluoromethanesulfonic acid and initiation by the latter in the polymerization experiments with triflate 4.

Finally, the polymerization of p-methoxystyrene initiated by p-nitrobenzenediazonium tetrafluoroborate 5 was repeated in the presence of the proton trap 2,4,6-tri-t-butylpyridine. A five-fold molar excess of the proton trap was used compared to initiator. A slightly lower yield of polymer was obtained (78%), but with identical molecular weight (1,800,000 by GPC). This excludes initiation by acidic impurities.

Discussion

Nitro-substituted aromatic halides, sulfonates and diazonium salts are initiators for cationic polymerization of widely varying activities. Compounds 1-3 showed low activity, while the triflate derivative 4 was moderately active. For these compounds, the reactions are believed to occur through an addition-elimination mechanism as shown in Figure 1.



$X = F,\ Cl,\ OSO_2C_6H_4CH_3\text{-}p,\ OSO_2CF_3$

Figure 1: Reaction scheme for initiation of p-methoxystyrene by initiators 1-4.

For the extremely reactive p-nitrobenzenediazonium tetrafluoroborate 5, an analogous reaction scheme can be proposed (Figure 2).

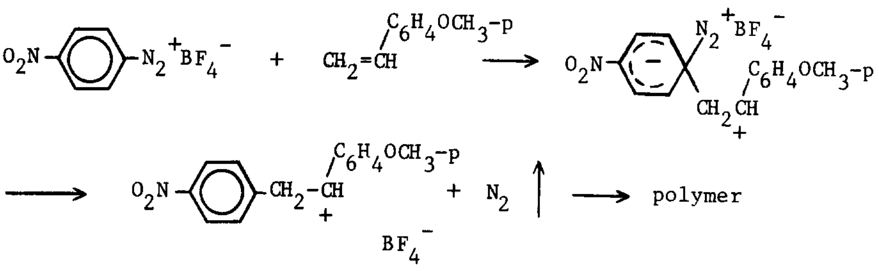


Figure 2: Initiation by p-nitrobenzenediazonium tetrafluoroborate.

The order of efficiency of these initiators, 5>>4>>3>2>1, is the same as the order of leaving group abilities, and the reverse order of decreasing nucleophilicity. The very nucleophilic counterions, such as F^-, are more likely to participate in subsequent termination reactions by recombination.

The remarkable entry is the last item, namely the diazonium salt. We were surprised that a search of the literature did not reveal any entries of thermal initiation of cationic polymerization by aryl diazonium compounds.[2] Nevertheless, by analogy with compounds 1-4, the mechanism in Figure 2 is proposed. In this tentative interpretation, the nitro group plays a key role in reducing the electron-density of the aromatic ring and permitting attack by the electron-rich olefin.

In conclusion, we have shown that activated aromatic diazonium compounds, sulfonates and halides can act as initiators for the cationic polymerization of the nucleophilic monomer p-methoxystyrene via a nucleophilic aromatic substitution mechanism. Polymer yields and molecular weight increased as the relative leaving group ability of the substituent increased. Compound 5, which contains the foremost leaving groups N_2^+ and the non-reactive counterion BF_4^-, was the best initiator giving immediate quantitative conversion to polymers with high molecular weights. Compound 4, which contains the excellent leaving group trifluoromethanesulfonate, was also an effective cationic initiator.

Acknowledgements

Support of this research by the National Science Foundation, Grant # DMR-81-06018, is gratefully acknowledged.

---

[2] The only exception is the p-chlorobenzenediazonium hexafluorophosphate initiated polymerization of tetrahydrofuran (Dreyfuss and Dreyfuss, 1966). However in this case hydride transfer is thought to be the initiation mechanism.

References

Bunnett, J. F. and J. Y. Bassett. J. Am. Chem. Soc. 81, 2104 (1959).

Chapman, T. M. and E. A. Freedman. Synthesis 11, 591 (1971).

Dreyfuss, M. P. and P. Dreyfuss. J. Polym. Sci. A4, 2179 (1966).

Parrett, F. W. and M. S. Sunn. J. Chem. Educ. 54, 488 (1977).

Zollinger, H. J. Am. Chem. Soc. 98, 3301 (1976).

Accepted September 25, 1984