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BOND FORMING INITIATION FOR CATIONIC POLYMERIZATION

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BOND FORMING INITIATION FOR CATIONIC POLYMERIZATION

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Professor of Chemistry

5-2-83
Date

DEDICATION

To my wife Roxanne for her patience and understanding.

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ABSTRACT

A new series of highly reactive organic initiators has been discovered. Five electron-poor aromatic compounds were used as "bond forming initiators" for the cationic polymerization of the electron-rich monomer p-methoxystyrene. p-Nitrobenzenediazonium tetrafluoroborate, 2,4-dinitrobenzene-1-trifluoromethanesulfonate and 2,4-dinitrobenzene-1-p-toluenesulfonate were prepared by literature methods. 1-Chloro-2,4-dinitrobenzene and 1-fluoro-2,4-dinitrobenzene were commercially available.

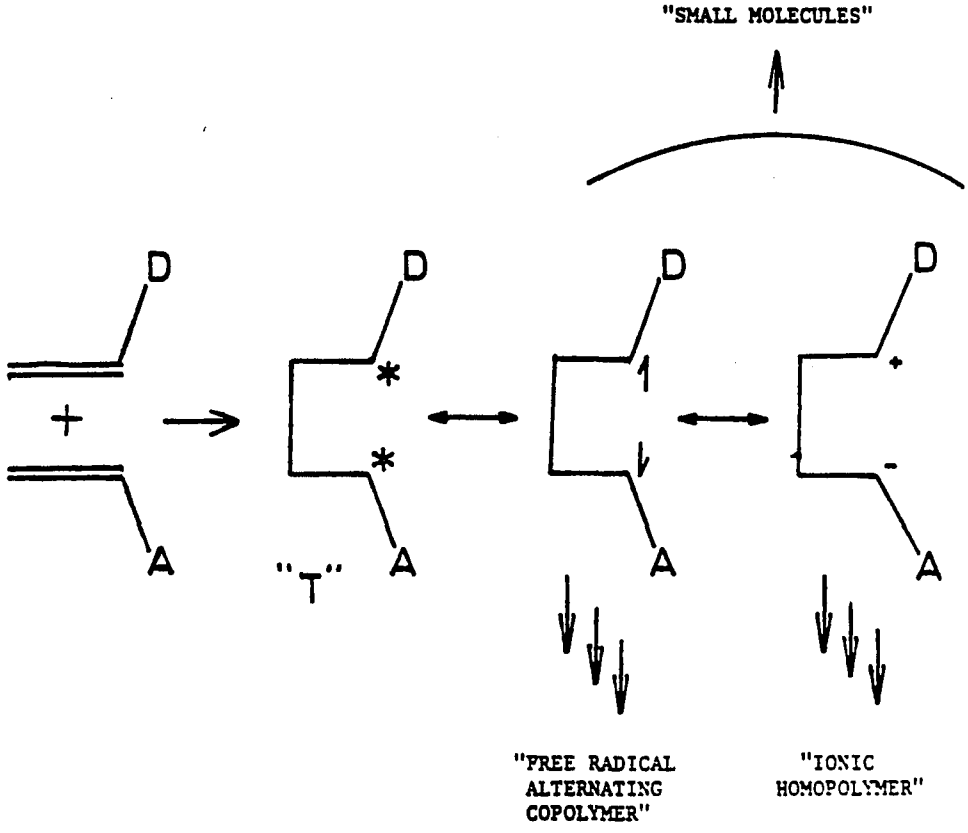
Polymer yields and molecular weights increased as the relative leaving group abilities of the 1-substituents increased. Gel permeation chromatography (GPC) was used to determine polymer molecular weights, which ranged from 10,000 to 1,700,000 ($\overline{M_w}$), and percent conversions.

The mechanism of initiation when electrophilic olefins are used as cationic initiators proceeds through a tetramethylene intermediate with predominantly zwitterionic character. It is proposed that tetramethylene theory be expanded to include tetramethylenes with the electron-poor terminal carbon atom as part of an aromatic ring. Competing reactions leading to small molecules are inhibited by this type of tetramethylene.

CHAPTER 1

INTRODUCTION

The spontaneous addition and polymerization reactions of electron-rich and electron-poor olefins leads to a remarkable variety of products. The mechanistic interpretation of this chemistry involves the formation of a key tetramethylene intermediate, T, generated by bond forming initiation (1). The tetramethylene is shown with the non-committal designation, *, to signify that it is a resonance hybrid of a spin paired biradical and zwitterionic form (2).



The predominant character of the tetramethylene is determined by the nature of the donor and acceptor substituents, D and A, respectively. Highly electron-donating and strongly electron-withdrawing substituents like alkoxy and cyanide, respectively, favor a predominately zwitterionic tetramethylene. Moderately electron-donating and electron-withdrawing substituents like phenyl and carbomethoxy, respectively, favor a predominately spin-paired biradical tetramethylene (3).

The tetramethylene can undergo a variety of reactions with products ranging from small molecules to high polymers. Some of the small molecules formed are cyclobutanes, cyclohexanes, 1-butenes and butadienes (4-7).

Trapping of the Tetramethylene Intermediate

Trapping of the tetramethylene would obviously provide excellent evidence to support its existence. There are many examples in the literature of both forms of the tetramethylene being trappable (8, 9).

The spin-paired biradical form of the tetramethylene will undergo free radical alternating copolymerization of each olefin. The zwitterionic form will initiate ionic homopolymerization of one or the other olefin. Using a tetramethylene to initiate a polymerization reaction is an extremely effective way of trapping the tetramethylene (10). This technique has two great advantages. First,

amplification: a very small amount of tetramethylene will lead to formation of an entire polymer chain. Secondly, diagnosis of the resulting polymer would indicate what the prevalent form of the original tetramethylene was. Homopolymer of either of the olefins would indicate a predominately zwitterionic form, while an alternating copolymer of the two olefins would indicate a predominately biradical form.

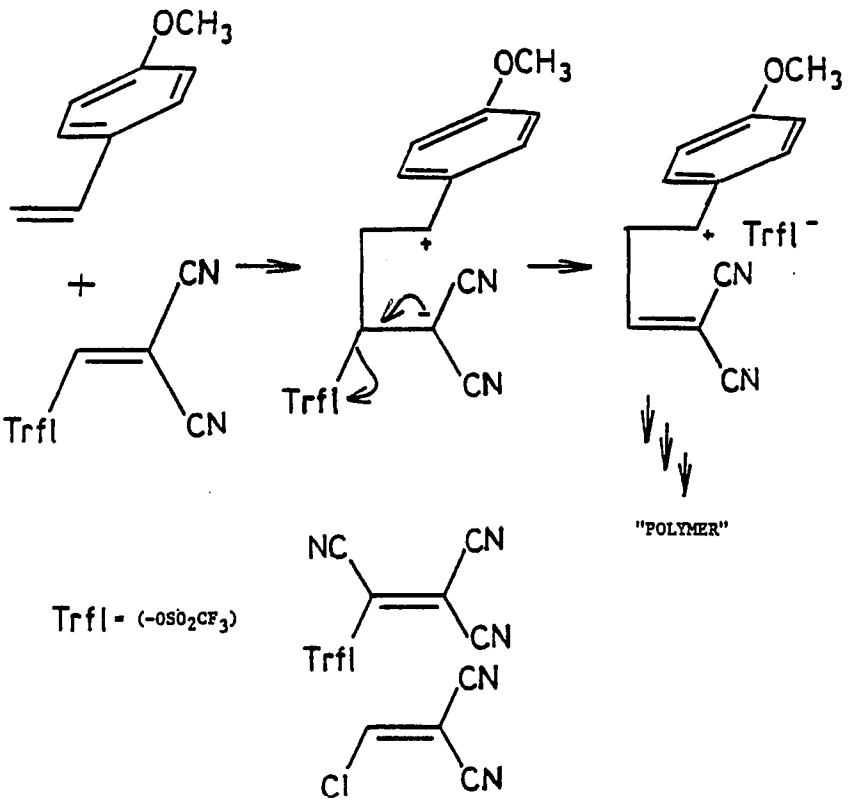
The Tetramethylene as a Cationic Initiator

Formation of a zwitterionic tetramethylene via bond forming initiation is an easy way to generate a cationic center. This suggests use as an initiator for cationic polymerization. However, the anionic end would probably interfere (11).

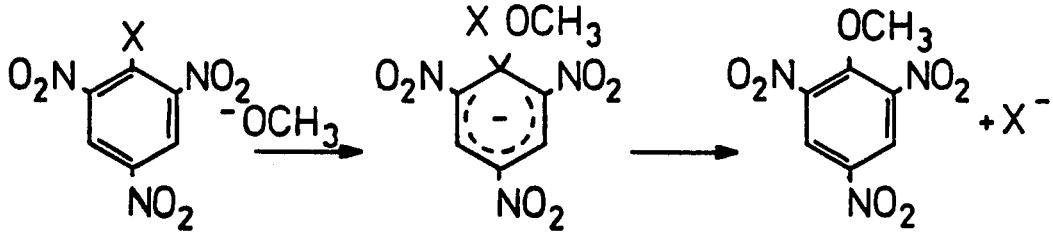
Stille, Tarvin, and Aoki (12) have shown that if the anion is highly resonance stabilized it will not interfere with cationic propagation. If the anion is extremely sterically hindered it will also limit anionic interference.

It has been shown in the reaction of 1,2,2-tricyanovinyl chloride with p-methoxystyrene to form 1,2,2-tricyano-4-(p-methoxyphenol)-butadiene that 1,4-zwitterions can expel a stable anion (7). Hall and Rasoul (13) have recently used this chemistry to synthesize efficient cationic initiators. 1,1-Dicyanovinyl trifluoromethane-sulfonate, and similar compounds, were used as cationic

initiators for the electron-rich monomer p-methoxystyrene. After formation of the tetramethylene the anion can lose the adjacent triflate group leaving a β-unsaturated ion-pair capable of cationic chain propagation. Utilization of this technique limits interference of the anion and inhibits the competing formation of small molecules. Rasoul obtained high polymers in quantitative yields even at very low initiator concentrations.



Nucleophilic attack on "activated" aryl halides and sulfonates (SnAR mechanism) has been known since the isolation of Meisenheimer Salts in 1902 (14). This is a two-step mechanism which involves the initial attack of the nucleophile to give the "Meisenheimer Salt," followed by the loss of the leaving group to yield the final substituted product. Usually the attack of the nucleophile is rate determining, but this is not always the case.



These types of highly electrophilic aromatic compounds are capable of forming tetramethylene-like intermediates with one of the terminal carbons of the tetramethylene in an aromatic ring. The presence of this aromatic nucleas prevents the formation of small molecules. For example, the fused bicyclic cyclobutane product would have high ring strain and result in the loss of "aromaticity" of the ring.

Present Work

In this work a series of electrophilic aromatic compounds was synthesized and evaluated as cationic initiators for the polymerization of the electron-rich

monomer p-methoxystyrene. The compounds were p-nitrobenzenediazonium tetrafluoroborate, 1, 2,4-dinitrobenzene-1-trifluoromethanesulfonate, 2, 2,4-dinitrobenzene-1-p-toluenesulfanate, 3, 1-chloro-2,4-dinitrobenzene, 4, and 1-fluoro-2,4-dinitrobenzene, 5. Compounds 1-3 were synthesized in the laboratory while 4 and 5 were commercially available.

The ability of a zwitterionic tetramethylene to lose a stable anion, as well as the new concept of extension of tetramethylene theory into the aromatic realm, were both utilized to enhance yields of high polymer and inhibit small molecule formation.

GPC determinations of polymer molecular weight and percent conversion as a function of time were used to compare the effectiveness of each initiator compound. The results were explained in terms of the relative gegenion reactivities of compounds 1 through 5. A plot of molecular weight versus reaction time using initiator 2 was discussed.

CHAPTER 2

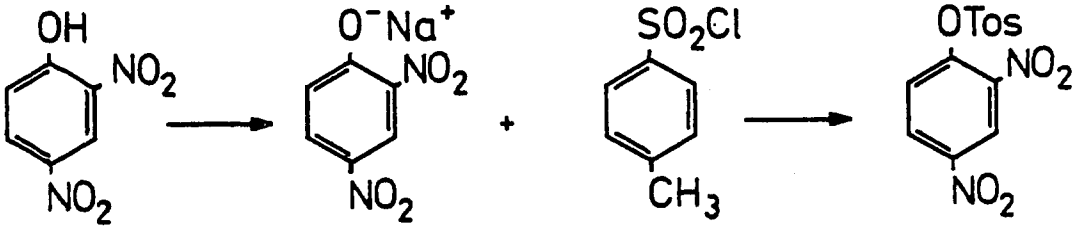
RESULTS

A series of electron-poor aromatic molecules with leaving groups in the 1-substituent position was synthesized and found to be cationic initiators for the electron-rich monomer p-methoxystyrene. Two of the five molecules were found to be highly effective cationic initiators. A correlation is shown between polymer yields and molecular weights and the relative gegenion reactivities of the 1-substituents.

Synthesis of Electron-Poor Aromatics

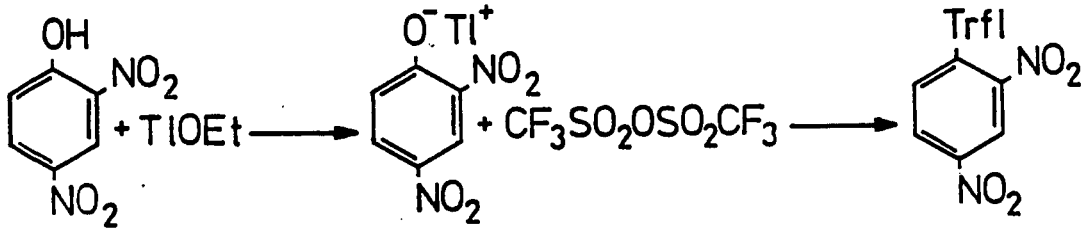
2,4-Dinitrobenzene-1-p-toluenesulfonate, 3

This compound was prepared by the method of Bunnett and Bassett (15).



2,4-Dinitrobenzene-1-trifluoromethane-sulfonate, 2

With a few modifications, this compound was synthesized by the method of Chapman and Freedman (16). Mechanical stirring was used in the anhydride reaction rather than magnetic stirring. The dichloromethane solvent was flash-evaporated and the oil that remained redissolved in carbon tetrachloride and treated with activated charcoal instead of being treated with charcoal in the dichloromethane. Finally, the second recrystallization of the product was from carbon tetrachloride/benzene (5 to 1) rather than absolute ethanol.

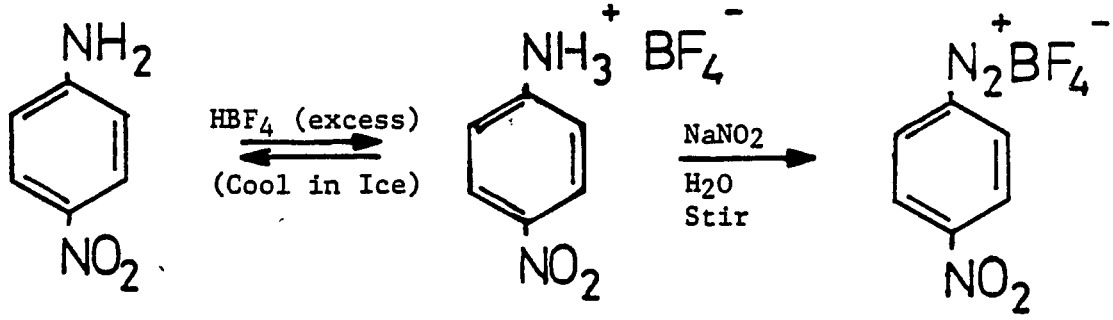


The authors mention that the reactions of sodium 2,4-dinitrophenoxide and 2,4-dinitrophenol with trifluoromethanesulfonic anhydride resulted in only a very low yield of the desired product. That is why the thallium salt method is recommended.

p-Nitrobenzenediazonium Tetrafluoroborate, 1

It is crucial that the final product be washed thoroughly in cold fluoboric acid, water, ethanol and

ether, respectively, to remove any residual starting material or impurities.



Electron-poor Aromatics as Cationic Initiators of p-Methoxystyrene in Nitromethane

1-Fluoro-2,4-dinitrobenzene, 5

This compound was a less reactive cationic initiator than compounds 1-4. In solution high initiator concentrations were necessary to obtain low yields of polymer (Table 1). At 10 mole % initiator only 0.13% of the initiator was used to begin a polymer chain (Table 8, p. 22). All of these polymerization solutions maintained a persistent yellow color. The molecular weight ($\overline{M_w}$) of the polymer obtained was 10,000 (Table 7, p. 20). No polymer was produced in bulk reactions.

1-Chloro-2,4-dinitrobenzene, 4

This compound was slightly more effective as a cationic initiator than compound 5. This was due to the lower reactivity of chloride gegenion in chain termination

Table 1. 1-Fluoro-2,4-dinitrobenzene as initiator for p-methoxystyrene polymerization in nitromethane.

(M)[a]	%I[b]	Time (h)	Temp. (°C)	% Yield[c]
2.51	10	4	101-108	--
2.51	10	24	101	1
1.88	25	15	101-120	20
Bulk	10	4	100-108	--
Bulk	10	24	101	--

[a]Monomer concentration in moles per liter.
[b]Mole percent initiator.
[c]Based on conversion of monomer to polymer.

reactions in nitromethane solvent. In solution lower initiator concentrations could be used to obtain slightly higher yields of polymer (Table 2). Reaction solutions were always a persistent yellow color. At 3 mole % initiator 8.6% of it was used to initiate a polymer chain (Table 8, p. 22). The molecular weight of the polymer obtained ($\overline{M_w}$) was 16,000 (Table 7, p. 20). No polymer was produced in bulk reactions.

2,4-Dinitrobenzene-1-p-toluenesulfonate, 3

Due to the better leaving group ability and the lower gegenion reactivity of the 1-OTos substituent, this compound was a more effective cationic initiator than compounds 4 and 5. Less time was required to obtain

Table 2. 1-Chloro-2,4-dinitrobenzene as initiator for p-methoxystyrene polymerization in nitromethane.

(M)[a]	%I[b]	Time (h)	Temp. (°C)	% Yield[c]
2.51	3	6.5	101	--
2.51	3	15	101	14
2.51	3	24	101	30
Bulk	6	168	80	--
Bulk	6	3	170	--

[a]Monomer concentration in moles per liter.

[b]Mole percent initiator.

[c]Based on conversion of monomer to polymer.

equivalent polymer yields. This indicates a faster initiation rate for compound 3 than 4 and 5 (Table 3). At 5 mole % initiator 5.3% of it was used in the polymerization reaction (Table 8, p. 22). The molecular weight ($\overline{M_w}$) of the resulting polymer was 22,000 (Table 7, p. 20).

2,4-Dinitrobenzene-1-trifluoromethanesulfonate, 2

This compound was far more reactive than compounds 3-5. Using compound 2 as cationic initiator gave 50%-60% conversion in 2-2.5 hours indicating a much faster rate of initiation (Table 4). The triflate group is the best organic leaving group known and it is the least reactive gegenion mentioned so far. For the first time, compound 2

Table 3. 2,4-Dinitrobenzene-1-p-toluenesulfonate as initiator for p-methoxystyrene polymerization in nitromethane.

(M)[a]	%I[b]	Time (h)	Temp. (°C)	% Yield[c]
1.71	5	7.5	100-102	2
1.50	5	20	102-106	14
1.71	5	26	100-102	44
1.50	5	48	102-106	82

[a]Monomer concentration in moles per liter.

[b]Mole percent initiator.

[c]Based on conversion of monomer to polymer.

[d]Reaction was not tried in bulk.

Table 4. 2,4-Dinitrobenzene-1-trifluoromethanesulfonate as initiator for p-methoxystyrene polymerization in nitromethane.

(M)[a]	%I[b]	Time (h)	Temp. (°C)	% Yield[c]
1.25	5	3.5	22	--
1.25	5	2	101	56, 58
1.25	5	2.5	100-102	50, 60
1.71	5	7.5	100-102	Quant.
Bulk	5	15	110	81

[a]Monomer concentration in moles per liter.

[b]Mole percent initiator.

[c]Based on conversion of monomer to polymer.

gave high yields of polymer in bulk conditions. In solution the polymer molecular weight ($\overline{M_w}$) was 82,000 (Table 7, p. 20). At 5 mole % initiator 1.9% of it was used to initiate a polymer chain (Table 8, p. 22).

In both solution and in bulk a persistent yellow color was observed throughout these polymerization reactions.

GPC was used to generate a conversion plot for compound 2 (Figure 1). This plot showed excellent reproducibility between two identical side by side reactions. The initial deviation of the data points in the first portion of these curves was due to the initial presence of some type of impurity, probably water, retarding the conversion of monomer to polymer.

A GPC plot of an aliquot of the polymerization solution after 180 minutes of reaction time is shown in Figure 2. This plot shows the absence of small molecules in the system and illustrated the unimodal molecular weight distribution.

The GPC data were used to calculate a plot of molecular weight versus reaction time for compound 2 (Figure 3). There was an initial inhibition of polymer molecular weight, probably caused by trace impurities, followed by a maximum molecular weight and then a gradual reduction as reaction time increased. The molecular weight reduction was due to the decreasing monomer concentration.

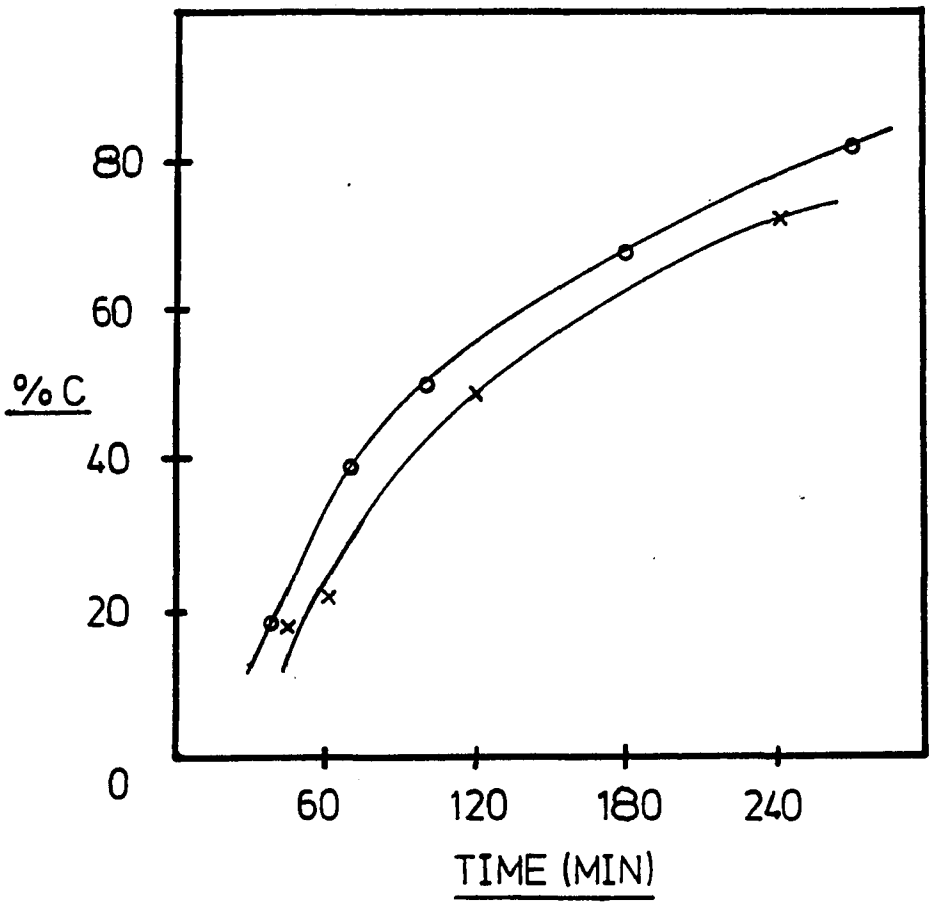


Figure 1. Conversion curve for polymerization of p-methoxystyrene with 2,4-dinitrobenzene-1-trifluoromethanesulfonate as cationic initiator -- Percentage conversions calculated by GPC. o, x represent two identical reactions.

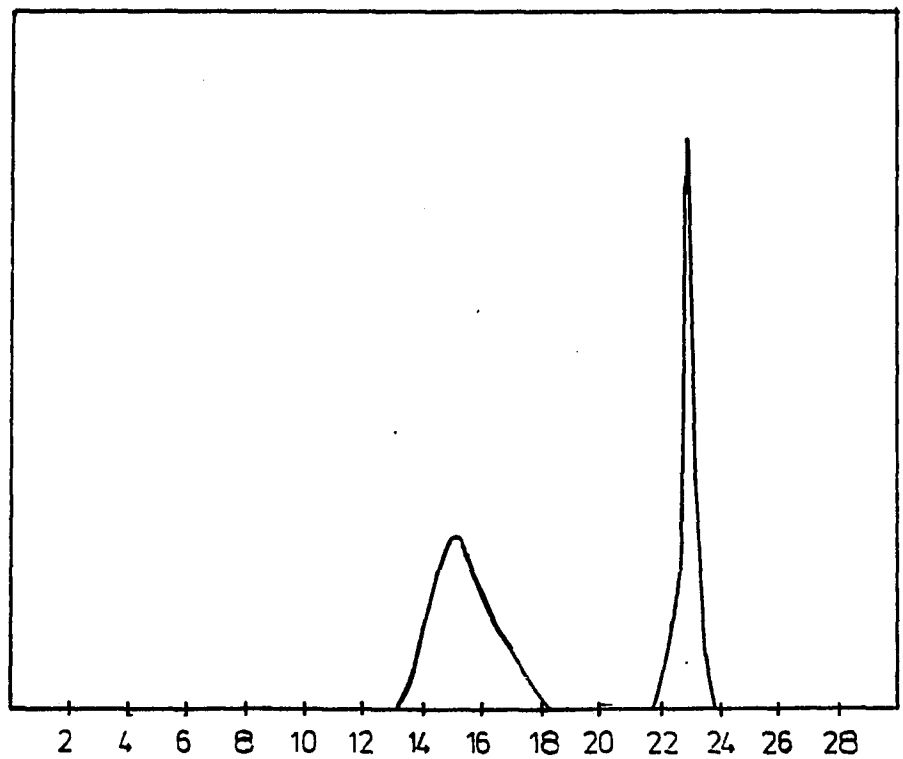


Figure 2. Gel permeation chromatogram of p-methoxystyrene polymerization with 2,4-dinitrobenzene-1-trifluoromethanesulfonate as cationic initiator -- Aliquot taken after 180 minutes of reaction time. Elution time of 13-18 minutes and 22-24 minutes was polymeric material and residual monomer, respectively.

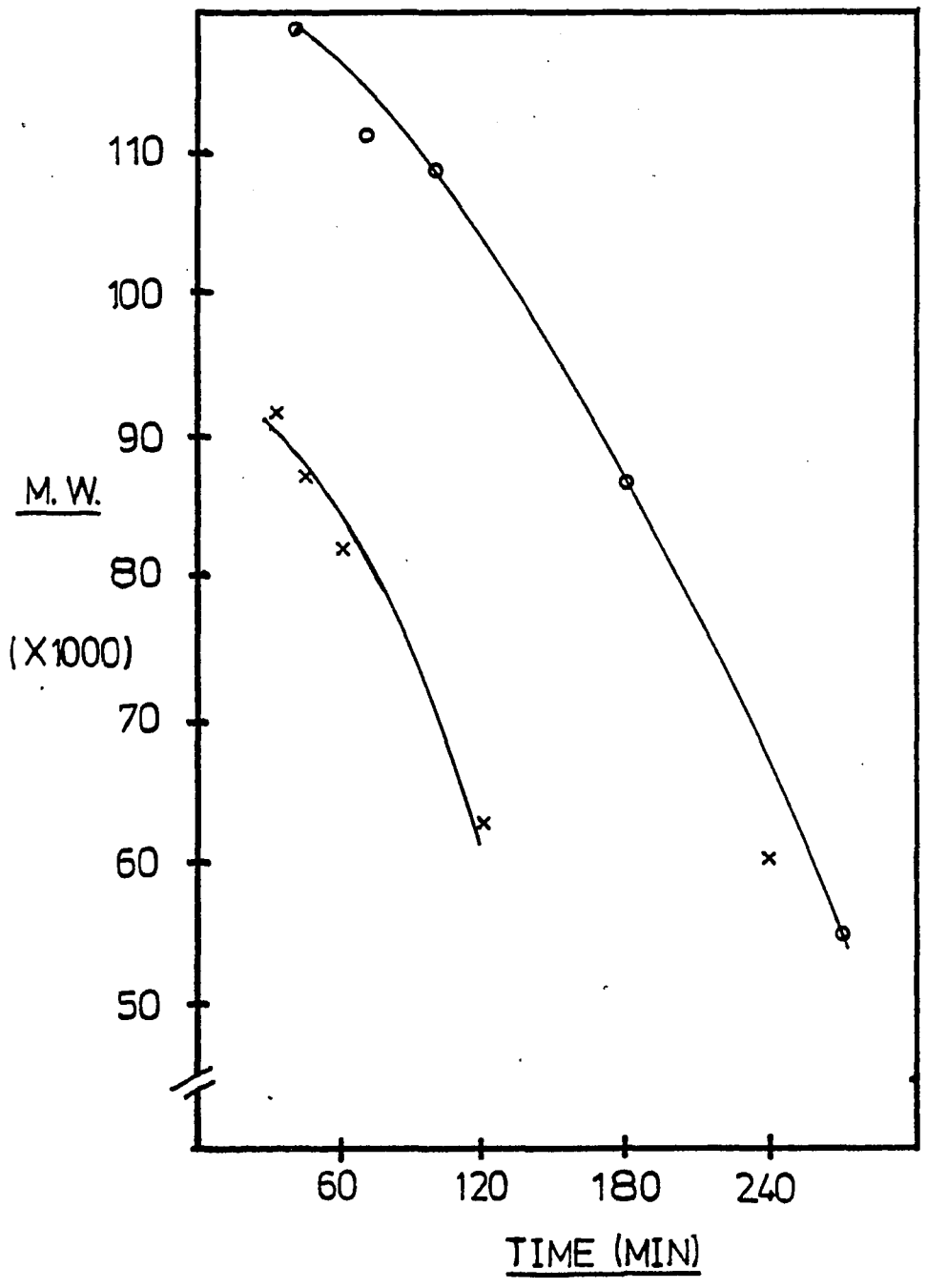


Figure 3. Plot of molecular weight versus reaction time using 2,4-dinitrobenzene-1-trifluoromethane-sulfonate as initiator for p-methoxystyrene polymerization -- o, x represent two identical reactions.

p-Nitrobenzenediazonium Tetrafluoroborate, 1

This compound was an excellent cationic initiator for p-methoxystyrene. In solution and in bulk, at room temperature there was immediate quantitative conversion of monomer to polymer, even at initiator concentrations of less than 0.01% (Table 5). The reactions were so exothermic they could not be controlled.

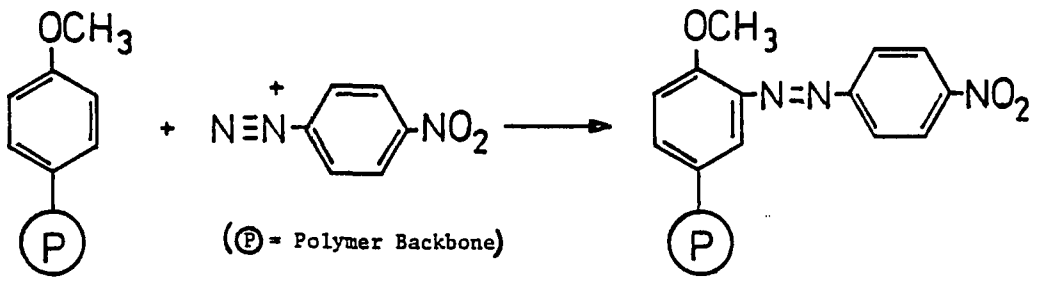
Table 5. p-Nitrobenzenediazonium tetrafluoroborate as initiator for p-methoxystyrene polymerization in nitromethane.

(M)[a]	%I[b]	Time (min)	Temp. (°C)	% Yield[c]
1.25	5	Imm.[d]	R.T.[e]	Quant.[f]
Bulk	5	Imm.	R.T.	Quant.
1.25	.01	Imm.	R.T.	Quant.
Bulk	.009	Imm.	R.T.	Quant.

[a]Monomer concentration in moles per liter.
[b]Mole percent initiator.
[c]Based on conversion of monomer to polymer.
[d]Immediate reaction.
[e]Room temperature.
[f]Quantitative yield: polymerized to a solid.

The nitrogen leaving group of compound 1 is an even better leaving group than the triflate moiety of compound 2. Using only 0.01% of compound 1 as initiator in a polymerization reaction resulted in 80% of it being utilized to initiate a polymer chain (Table 8, p. 22). The molecular weight of this polymer ($\overline{M_w}$) was over one million (Table 7, p. 20). A persistent violet color was observed in all of these polymerization reactions.

A model reaction using anisole and compound 1 in nitromethane solvent formed this violet color. If compound 1 is added to a stirring solution of pure white poly-p-methoxystyrene in nitromethane the isolated polymer is violet in color. When very low concentrations of compound 1 are used the resulting polymer is white. When an excess of compound 1 is used (5%) even after multiple reprecipitations, the resulting polymer is violet in color. These facts strongly suggest that residual diazonium initiator is undergoing an electrophilic aromatic substitution with the electron-rich benzene rings in the polymer backbone.



Elemental analysis of this violet colored polymer showed 0.07% nitrogen. The molecular weight of this polymer was so high (Table 7, p. 20) that this percentage of nitrogen in the polymer could not have arisen from the nitro group on compound 1 alone. Nitrogen of the diazo linkage must also be present.

Using 1% of compound 1 as initiator for p-methoxystyrene and 3% triphenylphosphine as cationic inhibitor formed no polymer. When 2% of a free radical inhibitor was used, bis-(4-hydroxy-3t-butyl-5-methylphenyl)-sulfide, homopoly-p-methoxystyrene was obtained in quantitative yeild at room temperature.

Exclusion of a Purely Thermal and an Acidic Impurity Initiation Process

p-Methoxystyrene in nitromethane solvent was heated for 24 hours under identical reaction conditions as a typical polymerization run. This experiment resulted in only a 2% yield of polymer of molecular weight ($\overline{M_w}$) of 7,000 (Table 6). The yield of this reaction is too low to make it a significant contributor to the overall polymer yields. The molecular weight of this polymer is also lower than the molecular weights of any of the polymers obtained using compounds 1-5 (Table 7).

A reaction using 10% 2,4-dinitrophenol as the initiating species resulted in only a 7% yield of polymer (Table 6). This acidic impurity could have arisen from the

Table 6. Exclusion of acidic impurities and a purely thermal initiation process.[a]

(M)[b]	%I[c]	Time (h)	Temp. (°C)	%P[d]	$\overline{M_w}$ (GPC)[e]
2.51	--	24	101	2	7000
1.88	10.3	19	100-102	7	19000

[a] 2,4-Dinitrophenol as acidic impurity.

[b] Concentration of monomer in moles per liter.

[c] Mole percent initiator.

[d] Percentage yield of polymer.

[e] Molecular weights calculated from polystyrene calibration curve.

Table 7. Initiator reaction summary and molecular weights of polymers obtained.[a]

I[b]	%I[c]	Time (h)	Temp. (°C)	% Yield[d]	$\overline{M_w}$ (GPC)[e]
F^-	10	24	101	1	10,000
Cl^-	3	24	101	30	16,000
$OTos^-$	5	26	100-102	44	22,000
$Trfl^-$	5	2	101	56	82,000
$N_2^+BF_4^-$	5	Imm.	R.T.	Quant.	644,000
$N_2^+BF_4^-$	.01	Imm.	R.T.	Quant.	1,700,000

[a] All monomer concentrations between 1.25 and 2.50 M/L.

[b] Initiator gegenion.

[c] Mole percent initiator.

[d] Based on conversion of monomer to polymer.

[e] Molecular weights calculated using polystyrene calibration curve.

hydrolysis of any one of the compounds 1-5. Once again, the yield of polymer in this reaction is too low to make it a significant contributor to the overall yields of polymer in this research.

Table 8. Summary of initiator efficiencies in the polymerization of p-methoxystyrene in nitromethane.

I Initiator Gegenion	Mole % I	% Yield Polymer	Moles Monomer Consumed[a] ($\times 10^{-3}$)	$\overline{M_w}$ (GPC)	D_p (GPC)[b]	Moles I Consumed[c] ($\times 10^{-6}$)	I Efficiency F%[d]
F^-	10	1	0.0376	10,000	75	0.50	0.13
Cl^-	3	30	1.13	16,000	119	9.50	8.42
$OTos^-$	5	44	1.65	22,000	164	10.0	5.32
$Trfl^-$	5	58	2.18	82,000	611	3.57	1.90
$N_2^+BF_4^-$	5	100	3.76	644,000	4,799	0.783	0.42
$N_2^+BF_4^-$	.01	100	3.76	1,700,000	12,670	0.297	79.00

[a] Based on 0.5 ml or 3.76×10^{-3} moles of monomer.

[b] Molecular weight monomer = 134.18 g/m.

[c] Moles of monomer consumed/D_p.

[d] (Moles of I consumed/Moles of I initially) x 100 = percentage of initiator used for polymerization reaction assuming no chain transfer.

CHAPTER 3

DISCUSSION

The predominant character of the tetramethylene formed in a particular electron-rich electron-poor reaction will determine the course of the reaction and the type of product produced in the reaction. Reactions between olefins that contain strong donors, like p-methoxystyrene or vinyl ether, and olefins that contain strong acceptors, like vinylidene cyanide or nitroethylene favor tetramethylenes with zwitterionic character (17). In this research donors and acceptors that favored zwitterionic tetramethylenes were selected so that cationic homopolymerization could be studied.

The tetramethylene can undergo undesirable side reactions to form various small molecules, for example, tetramethylene closure to form cyclobutanes or a β elimination to yield an alkene (18).

Rasoul (11, p. 43) has shown that the anionic center of a zwitterionic tetramethylene can be eliminated by the loss of a β leaving group and that this effectively inhibits small molecule formation while enhancing cationic polymerization. In this research addition of an aromatic nucleus into the electron-poor portion of the tetramethylene, as well as incorporation of the β leaving group concept, further

enhance cationic polymerization. Formation of a cyclobutane is now specifically inhibited because it would result in the loss of aromaticity of the aromatic nucleus and a strained fused bicyclic system. Two factors have been introduced into the tetramethylene intermediate which enhance the desired cationic polymerization and inhibit the competing small molecule formation.

These concepts can also be viewed as a use of aromatic compounds activated to nucleophilic substitution reactions as cationic initiators.

Cationic Initiators

A new class of organic initiators for cationic polymerizations was discovered. Compounds 1 and 2 were highly effective. The mechanism of this initiation has been entitled "Bond Forming Initiation." The series of compounds 1 through 5 are arranged in order of expected decreasing electrophilicity and expected decreasing leaving group ability. The results obtained support these expectations. The compounds elected for study in this research were the 2,4-dinitrobenzene-1-substituent systems.

The reactions are believed to occur according to the reaction scheme shown in Figure 4.

There were two main considerations in choosing the 1-substituents. First, how reactive is the gegenion in terminating the propagating polymer chain? For example, a β

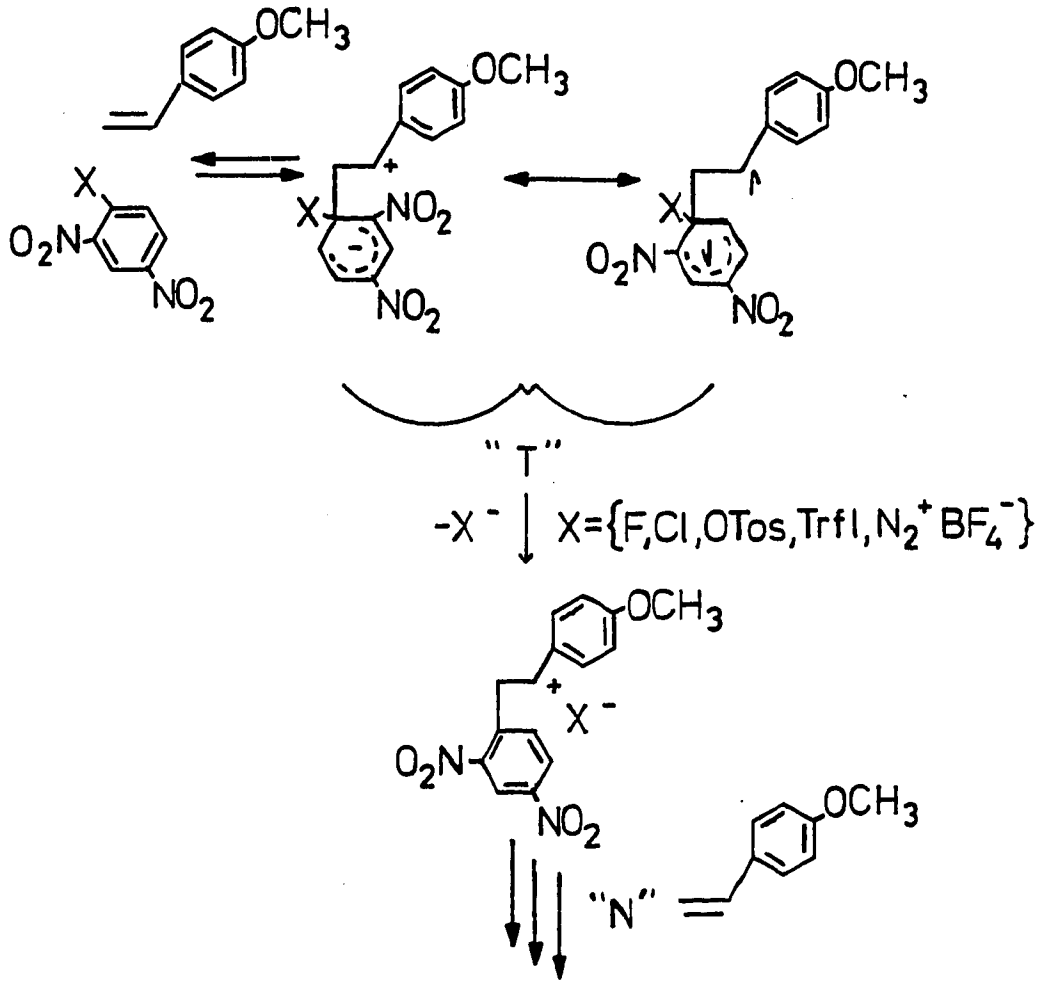


Figure 4. Reaction scheme for initiation of p-methoxystyrene polymerization in nitromethane -- $N_2^+BF_4^-$ species was p-NO_2 substituted only.

elimination would give a terminal unsaturation in the chain, or a recombination with gegenion to give a terminally saturated chain. Secondly, how good a leaving group is the 1-substituent? The mechanistic interpretation of this initiation is a nucleophilic displacement by the π-electrons of the electron-rich monomer on the carbon atom of the aromatic compound containing the 1-substituent. The relative leaving group ability of the 1-substituents decreases in the order:

$$N_2^+BF_4^- > F_3CSO_2O^- > p\text{-}H_3C(C_6H_4)\text{-}SO_2O^- > Cl^- > F^-$$

Elimination of ions in the right hand side of this series will proceed slower than elimination of ions on the left. Since initiation rates increase in the series from right to left, this suggests that the second step of the initiation is rate determining, not the initial attack of the monomer. Moreover, gegenions in the right side of the table are more likely to participate in subsequent termination reactions than ions to the left. Proceeding from right to left in the series polymer yields and molecular weights increase.

An alternate explanation of this trend is that proceeding from right to left in the series the electrophilicity of the compounds also increases. This would

account for the observed trend if the first step of the mechanism were rate determining.

Comparison of Reactivities of 1-Chloro-2,4-dinitrobenzene and 1-Fluoro-2,4-dinitrobenzene

Bunnett, Garbisch, and Pruitt (19) have studied the displacements of 1-substituents from 1-substituted-2,4-dinitrobenzenes by piperidine in methanol. The relative rates of reactions to form 2,4-dinitrophenyl-piperidine for the halogens were: F = 3300, Cl = 4.3, Br = 4.3 and I = 1.0. The faster reaction rate for the fluorine moiety is attributed to its superior electron-withdrawing character, relative to the other halogens. The carbon atom of the C-F bond was more positive than the carbon atom of the other carbon-halogen bonds, making it more susceptible to nucleophilic attack. Fluorine, the smallest of the halogens, would also minimize any steric hindrance in the reaction. Bunnett et al. collectively called these two effects the "element effect."

The "element effect" says that if the rate determining step of initiation were the attack of the nucleophile, compound 5 would have been a better initiator than compound 4. These experimental results are contrary to the "element effect." This is evidence supporting the second step of the mechanism, loss of the leaving group, as rate determining.

It is also suggested that the fluorine gegenion was more reactive than the chlorine gegenion in terminating the growing polymer chain in nitromethane solvent (20).

Choice of Polymerization Solvent

In ionic polymerization there are generally three types of propagating ions (Figure 5) (21). The contact ion pair has no solvent molecules between the gegenion and cation. The solvent separated ion pair is partially separated by solvent molecules and the free ions are totally separated by solvent. Even though these species are all in equilibrium with each other, the free ion concentration is always much lower than the combined ion pair concentration. However the free cation is so much more reactive than the ion pairs, even at very low concentrations, that they determine the overall rate of polymerization.

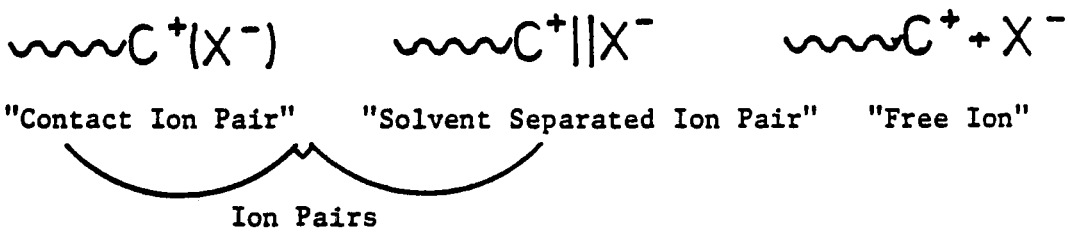


Figure 5. Propagating ion combinations in cationic polymerization.

Nitromethane is a very polar solvent (E_o = 33) and it gave a higher concentration of free ions due to solvation. The use of nitromethane polymerization solvent was expected to increase polymer yields and it was selected for use in this research.

Molecular Weight Versus Reaction Time Interpretation

Using the triflate molecule, compound 2, as cationic initiator for polymerization of p-methoxystyrene there was an initial inhibition of polymer molecular weight. This was followed by a maximum molecular weight and then a gradual reduction as reaction time increased. The initial inhibition of molecular weight was due to the presence of an impurity, probably water, terminating the propagating chains. In this system the initiation step is very slow. This means that there was constant introduction of new active species, cations, throughout the entire lifetime of the reaction. Initially, some of these new active species were terminated by the impurity resulting in a lower polymer molecular weight. As the impurity was used up and a new less effective termination reaction took over, the propagating chains grew to their maximum molecular weight. Molecular weight decreased with reaction time due to decreasing monomer concentration. As the propagating chains found it more difficult to find a molecule of monomer

to react with, the competing termination reaction became more and more favorable.

Exclusion of Purely Thermal, Acidic Impurity and Electron-Transfer Initiation Mechanisms

Each time a typical polymerization reaction was run using one of the compounds 1 through 5 as initiator, a blank reaction containing no initiator was run under identical conditions alongside it. In only one case did the blank reaction polymerize and these results were completely disregarded. This excludes the possibility of a purely thermal initiation process.

A reaction under identical conditions as a typical polymerization run with 10 mole percent 2,4-dinitrophenol as initiator, gave only a 7% yield of polymer. This acidic impurity could have arisen from the hydrolysis of any one of the compounds 1 through 5. The yield of polymer in this reaction was too low to make it a significant contributor to the overall yields of polymer. Molecular weights of polymers initiated with trifluoromethanesulfonic acid, the other hydrolysis product of compound 2, have been found to be lower than molecular weights of polymers obtained in this research (11, pp. 29-32). All polymers in this work, with the exception of a few initiated by compound 1, had unimodal molecular weight distributions (GPC). This excludes the possibility of an acidic impurity initiation process.

The possibility of an electron-transfer initiation mechanism will now be addressed. In this mechanism the electron-rich monomer donates an electron to the electron-poor initiator to form a p-methoxystyrene cation-radical and the initiator anion-radical. The cation radical then acts as the initiating species. Nishijima, Yamamoto, and Asanuma (22) report that in the presence of the electron acceptor, p-dicyanobenzene, generation of the p-methoxystyrene cation-radical in acetonitrile produced the trans-head-to-head cyclobutane dimer without producing any polymerized material. Hall and Abdelkader (23) also report formation of the cyclobutane dimer from p-methoxystyrene cation-radical. GPC analysis of polymer produced using compound 2 as initiator showed homopoly-p-methoxystyrene and no small molecules.

Using 1% of compound 1 as initiator and 3% triphenylphosphine as cationic inhibitor formed no polymer. A free radical inhibitor such as bis-(4-hydroxy-3-t-butyl-5-methylphenyl)-sulfide gave homopoly-p-methoxystyrene. This is strong evidence in support of a cationic initiation process.

CHAPTER 4

CONCLUSION

Zwitterionic tetramethylenes can be used as effective cationic initiators if elimination of the anionic center is possible. This occurs by loss of an adjacent leaving group to give a β-unsaturated ion pair capable of cationic propagation. Electron-poor aromatic compounds containing leaving groups in the 1-substituent position performed "bond forming initiation" with the electron-rich monomer p-methoxystyrene. This occurs by bond formation between the β carbon of the electron-rich olefin and the carbon atom which contains the 1-substituent in the electron-poor ring. Subsequent loss of the 1-substituent eliminates the anionic center of the zwitterion and allows propagation to begin. This suggests expansion of the tetramethylene theory to include tetramethylenes with the electron-deficient terminal carbon atom in an aromatic ring.

Another interpretation of these results was that activated aromatic halides, sulfonates and diazonium compounds can act as initiators for cationic polymerization via a nucleophilic aromatic substitution mechanism.

The yields and molecular weights decreased as gegenion reactivity increased. Compound 1, which contained

the excellent leaving group N_2^+ and the highly non-reactive gegenion BF_4^-, gave the highest polymer yields and molecular weights. Compound 2 which contained the excellent leaving group trifluoromethanesulfonate, was also a very effective initiator.

CHAPTER 5

EXPERIMENTAL

Instrumentation

All melting points and boiling points are uncorrected. Capillary melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were taken on Perkin-Elmer 398, 710A and 983 spectrophotometers. Proton nuclear magnetic resonance spectra were obtained on Varian EM-360 and T-60 spectrometers. Ultraviolet spectra were obtained on a Perkin-Elmer 552 spectrophotometer.

Gel permeation chromatography measurements were performed using an Altex pump, sp-8200 ultraviolet and Waters Associates R-401 refractive index detectors. Styragel 10^4 and 10^3 angstrom columns were used. Elemental analysis was performed by Micanal, Tucson, Arizona.

Solvents

Nitromethane was used as the polymerization solvent. It was purified as described by Parrett and Sunn (24). The solvent was dried by distillation from calcium hydride or barium oxide and stored under argon in a desiccator. The flask used was sealed with a ground glass stopcock, wrapped with parafilm and only opened in a glove bag under argon.

Other solvents were all commercially available reagent grade. Methylene chloride was distilled from calcium hydride immediately before use.

NMR solvents were from Norell, Inc. and all shifts are relative to TMS expressed in δ.

Monomer

p-Methoxystyrene (Aldrich) was distilled from calcium hydride at appropriate pressures and stored under argon in a desiccator at -10°C. The flasks used were sealed with ground glass stopcocks, wrapped with parafilm and only opened in a glove bag under argon.

Reagents and Chemicals

All chemicals used were reagent grade and commercially available. They were used as received, except where noted otherwise.

Electron-Poor Molecules

1-Fluoro-2,4-dinitrobenzene

This compound was commercially available from Aldrich. It was purified by multiple recrystallizations from ether (mp = 25.5-26.5°C).

1-Chloro-2,4-dinitrobenzene

This compound was commercially available from Aldrich. It was purified by multiple recrystallizations from ethanol (mp = 49.5-50.5°C).

2,4-Dinitrobenzene-1-p-toluenesulfonate

This compound was prepared by the reaction of sodium 2,4-dinitrophenoxide (2.64 grams, 0.013 moles) with p-toluenesulfonyl chloride (2.48 grams, 0.013 moles) as described by Bunnett and Bassett (15). The yield was 80% and the mp was 119-120°C.

2,4-Dinitrobenzene-1-trifluoromethanesulfonate

In a modification of Chapman and Freedman, after 24 hours of mechanical stirring of thallium-2,4-dinitrophenoxide (3.84 grams, 0.0099 moles) and trifluoromethanesulfonic anhydride (1.66 ml, 0.0099 mole) the dichloromethane solvent (135 ml) was flash evaporated leaving an oil (16). This oil was dissolved in carbon tetrachloride, treated with activated charcoal, filtered and set aside to recrystallize. After filtration, a second recrystallization from carbon tetrachloride-benzene (10/1) gave a 37% yield of yellow crystals (mp = 50-51.5°C).

p-Nitrobenzenediazonium Tetrafluoroborate

p-Nitroaniline (2.49 grams, 0.018 moles) was dissolved in the minimum amount of 49% fluoroboric acid.

After cooling to 0°C, an aqueous solution (2.5 ml) of sodium nitrite (1.23 grams, 0.018 moles) was added dropwise with constant stirring. The product was collected and washed with cold fluoboric acid, water, ethanol and ether, respectively. A 61% yield of tan crystals were dried in vacuo and stored in a desiccator under argon in the dark. This salt decomposes at 144-150°C.

General Reaction Procedure

All glassware was scrupulously cleaned with soap and water followed by multiple rinsing with distilled water, methanol, acetone and hexane, respectively. Reaction tubes were evacuated, fired with a bunsen burner and filled with argon gas. Syringes were baked in an oven at 110°C overnight before use. After cooling, all glassware was put into a glove bag which was then filled with argon.

Typical Polymerization Reaction

In a glove bag, a 3 ml syringe was used to transfer 0.5 ml of dry p-methoxystyrene (0.0038 mole) into each of 4 reaction tubes. A 10 ml syringe was used to dispense 3 ml of a dry nitromethane initiator solution (2×10^{-4} mole/3 ml) into 3 of the 4 reaction tubes. A 5 ml syringe was then used to transfer 3 ml of dry nitromethane into the remaining reaction tube. Finally each reaction tube was sealed with a three-way ground glass stopcock, removed from the glovebag and brought to the required reaction

temperature for the appropriate amount of time. Reaction tubes were wrapped in aluminum foil to exclude light and had constant magnetic stirring of the solutions within.

By applying a positive pressure of argon on one neck of the three-way stopcock, an aliquot could be syringed from the other neck without allowing air to enter the system.

The reaction mixture was added dropwise to approximately 100 ml of rapidly stirring methanol. The polymer was collected and reprecipitated from chloroform into methanol. After filtration, the isolated polymer was dried in vacuo at 50°C.

LIST OF REFERENCES

1. Salem, L., and C. Rowland. Angew. Chem. Intern. Ed. Engl., 1972, 11, 92.

2. Huisgen, R. Acc. Chem. Res., 1977, 10, 199.

3. Sentman, R. C. Thesis, University of Arizona, 1982, 24.

4. Hall, H. K., Jr., L. C. Dunn, and A. B. Padias. J. Org. Chem., 1980, 45, 835.

5. Hall, H. K., Jr., and P. Ykman. J. Am. Chem. Soc., 1975, 97, 800.

6. Glogowski, M., and H. K. Hall, Jr. J. Macromol. Sci. Chem., 1979, A13, 369.

7. Williams, J. K., D. W. Wiley, and B. C. McKusick. J. Am. Chem. Soc., 1962A, 84, 2210.

8. Huisgen, R., and S. Steiner. J. Am. Chem. Soc., 1973, 95, 5054.

9. Hall, H. K., Jr., and M. Gillard. Unpublished results, Chem. Dept., University of Arizona, 1981.

10. Hall, H. K., Jr. Angew. Chem. Intern. Ed. Engl., 1983, 4 (in press).

11. Rasoul, H. A. A. Thesis, University of Arizona, 1981, 11 and 12.

12. Stille, J. K., R. F. Tarvin, and S. Aoki. Macromolecules, 1972, 5, 66.

13. Hall, H. K., Jr., and H. A. A. Rasoul. Proceedings of the U.S.-Japan Polymer Meeting, Palm Springs, 1980, Dekker (in press).

14. March, J. In Advanced Organic Chemistry, 2nd Edition, McGraw-Hill, New York, 1977, pp. 584-586.

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

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

17. Hall, H. K., Jr. Angew. Chem., 1983 (in press).

18. Shirato, Y., J. Nagato, Y. Nakano, T. Nogami, and H. Mikowa. J. Chem. Soc., 1977, Perkin I, 14.

19. Bunnett, J. F., E. W. Garbisch, Jr., and K. M. Pruitt. J. Am. Chem. Soc., 1958, 79, 385.

20. Lowry, T. H., and K. S. Richardson. Mechanism and Theory in Organic Chemistry, 2nd Edition, Harper & Row, New York, 1981, pp. 284-285.

21. Odian, G. S. Principles of Polymerization, John Wiley & Sons, Inc., New York, 1981, pp. 341-360.

22. Nishijimi, Y., M. Yamamoto, and T. Asanuma. J. Chem. Soc. Chem. Comm., 1975, 53.

23. Hall, H. K., Jr., and M. Abdelkader. J. Org. Chem., 1981, 46, 2948.

24. Parrett, F. W., and M. S. Sunn. J. Chem. Educ., 1977, 54, 448.