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Setting the Stage: A Brief Introduction to Sterically Hindered Amines in Organic Chemistry and Scouting Experiments

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ABSTRACT

The precise tailoring of polymer molecules (macromolecular engineering) by cationic methods can only be achieved in the absence of adventitious protogenic events, i.e., uncontrolled initiation, chain transfer to monomer. It is postulated that these undesirable processes can be aborted in cationic polymerization charges by the use of certain sterically hindered amines. This group of compounds has been used to scavenge protons in preparative small molecule organic chemistry, the pertinent literature of which is briefly examined. Orienting polymerization experiments carried out in the presence of various sterically hindered amines, in particular with 2,6-di-tert-butylpyridine, gave encouraging results in terms of conversion, molecular weights, and molecular weight distributions, and gave impetus for further detailed investigations.

INTRODUCTION

For some time research in our laboratories has mainly been focused on macromolecular engineering (i.e., on the precise tailoring

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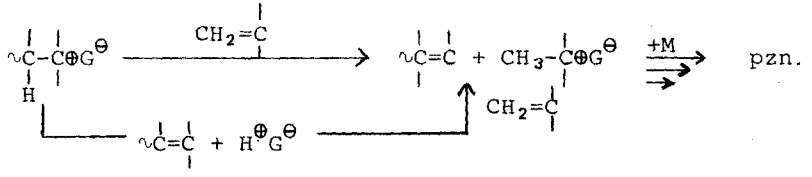
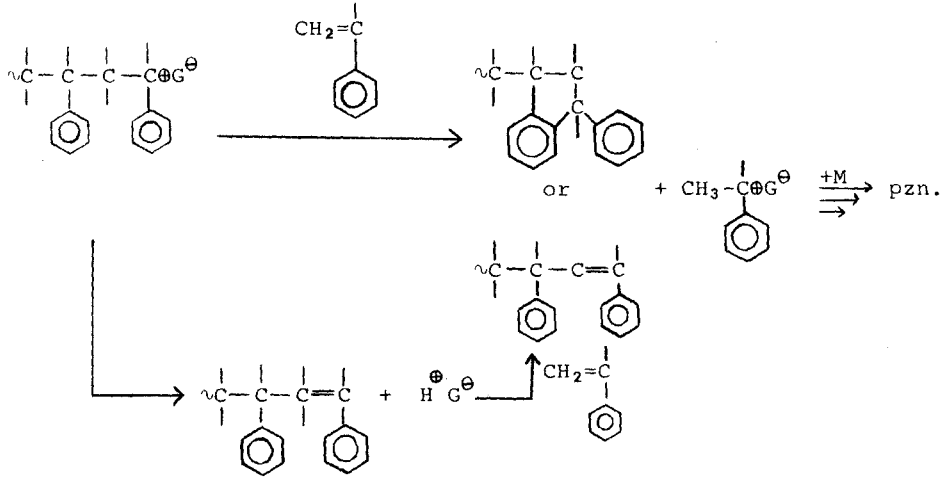
of polymer head groups, endgroups, repeat units, microstructures, substituents, molecular weights, molecular weight distributions, sequence distributions, branching frequencies, molecular weights between cross-linking sites, block, graft and radial star topologies, etc.) by cationic techniques. We are convinced that the most efficient way toward macromolecular engineering is by fundamental research directed toward the elucidation of the mechanism of polymerizations. Today we are in a good position to exploit our increased insight into the mechanistic details of cationic polymerizations for the tailoring of macromolecules with precisely defined architectures. For example, the development of controlled initiation has led to new grafts and bigrafts, and that of chain transfer to select chain transfer agents (i.e., the inifer technique) yielded new telechelic oligomers [1].

One of the undesirable aspects of macromolecular engineering by carbocationic techniques is chain transfer to monomer, i.e., the reaction which proceeds by proton elimination/reprotonation. In the presence of this reaction, one of the terminal units of the polymeric products will be an essentially nonfunctionalizable "sterile" CH_3- group. Depending on the particular type of the monomer employed, chain transfer to an aliphatic monomer results in a terminal olefin plus a CH_3– head group, whereas chain transfer to an aromatic monomer (i.e., styrene derivatives) yields a terminal indane skeleton plus a CH_3– head group:

Chain Transfer to Aliphatic Monomer:



Chain Transfer to Aromatic Monomer (Styrene Derivatives):



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Intramolecular cyclization (indane skeleton formation) can occur only with styrene and its derivatives (indene and acenaphthylene behave differently), and indeed this is the preferred route of chain transfer to monomer with these monomers.

In either case the end structures formed by these processes are most undesirable to the macromolecular engineer. First of all, the CH_3- head groups and/or terminal indane skeletons are unreactive (sterile) for further derivatization. Terminal olefin groups would be acceptable; however, they always form in conjunction with a saturated head group so that the resulting chain carries two dissimilar termini.

Another area where further advances would be most welcome is in the understanding and control of initiation. It appears that useful, functionalizable head groups can only be obtained in the absence of protic initiation by "controlled initiation," i.e., when the first cationation of the monomer is effected by a carbenium ion generated from a suitable cationogen in conjunction with certain specific Friedel-Crafts acids such as Et_2AlCl and BCl_3. Among the best examples of controlled initiation are the syntheses of sequential (graft and block) copolymers [1, 2], i.e., syntheses in which macrocarbenium ions ($P^{\oplus}$) generated from halogenated high polymers (PX) by the use of the aforementioned Friedel-Crafts acids (F.C.) initiate the polymerization of select monomers (M):

$$PX + F.C. \longrightarrow P^{\oplus} + F.C.X^{\ominus}$$

$$P^{\oplus} + M \rightleftharpoons P \sim M^{\oplus}$$

In contrast, in the presence of the vast majority of conventional Friedel-Crafts acids, e.g., $AlCl_3$, $SnCl_4$, $TiCl_4$, and BF_3, these graft copolymerizations are usually accompanied by homopolymer formation due to uncontrolled initiation by ubiquitous protogenic impurities and/or chain transfer to the monomer.

In the course of our extended fundamental studies directed toward the elucidation of the mechanism of carbocationic polymerizations, we theorized that sterically hindered bases (proton traps) could be employed to suppress chain transfer to monomer and to effect controlled initiation, and thus to produce 100% grafting and/or blocking efficiencies.

About 30 years ago Brown and Kanner [3, 4] discovered that the sterically crowded pyridine derivative 2,6-di-tert-butylpyridine (DtBP) exhibits extraordinary specificity toward reaction with proton (i.e., under conventional conditions DtBP reacts with HCl but not with BF_3 or CH_3I), and recognized that this sterically hindered pyridine base could be employed to distinguish between protic and Lewis acids. This seminal discovery has been followed up by a very

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large number of fundamental studies aimed at the elucidation of the basic proton trapping phenomenon on the one hand and on the exploitation of this specific effect for preparative purposes on the other hand [5-14]. Most notable among these investigations as far as we were concerned were those which demonstrated the very high basicity coupled with nonnucleophilicity of DtBP [3-14], the enormous rate of proton trapping by DtBP [13, 14], and the very high proton affinity of DtBP and related materials [9, 12, 15-17].

A careful reading of these literature references led us to postulate that in cationic polymerization systems these strong nonnucleophilic bases would enormously rapidly and specifically react with free protons but would not, however, interfere with elementary reactions that involve carbenium ions, i.e., controlled initiation and propagation. Thus the stage was set to commence experimentation with proton traps, first of all to determine whether cationic polymerizations are possible in the presence of sterically hindered bases, and if so, whether the proton that is transferred from the growing carbocation to the incoming monomer during chain transfer to monomer can be trapped. In light of the above survey we postulated that proton trapping by sterically hindered bases would abort chain transfer to monomer and uncontrolled initiation due to impurities ("H_2O"). We expected these bases to suppress if not eliminate cationation by (free) protons and/or reinitiation of the kinetic chain after proton elimination, and thus to prevent the formation of CH_3- head groups.

Further, the possibility of controlled initiation in open systems with conventional Friedel-Crafts acids arose. To date, controlled initiation can be carried out with conventional Friedel-Crafts acids only under cumbersome high-vacuum conditions in super-dry systems or with a few specific alkylaluminum compounds of BCl_3 (see above and Ref. 1).

The important practical impetus for research with proton traps was the possibility of augmenting cationic blocking and grafting efficiencies, hopefully to 100%, by the use of these chemicals (see above and Ref. 2). Blocking and grafting efficiencies are measures of the amount of blocked or grafted polymer relative to the homopolymer formed in an experiment, e.g., $G_{eff.} = P_g/(P_g + P_h)$, where $G_{eff.}$ is grafting efficiency and P_g and P_h are the weight of grafted branch and homopolymer, respectively. Since homopolymer formation in sequential copolymerizations is mostly due to chain transfer to monomer [1, 2], we theorized that we could eliminate the source of the by-product by the use of proton traps.

Last but not least, it was hoped that systematic experiments with proton traps will provide insight into important mechanistic details of cationic and other polymerization processes in general. The diagnostic value of proton traps appeared considerable not only for cationic polymerizations but for any polymerization systems, i.e., organometal-induced anionic or coordinated systems, in which protic impurities may affect the mechanism. For example, water

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has often been postulated to affect initiation in Ziegler-Natta polymerizations [18]; the use of proton traps may help to elucidate this problem.

SCOUTING EXPERIMENTS WITH STERICALLY HINDERED BASES [19]

With the above thoughts in mind, experiments have been designed to determine whether carbocationic polymerizations are possible in the presence of sterically hindered bases. Experimentation started in 1972 [20] whose aim was the t-butylation of 2,4,4-trimethyl-1-pentene (TMP) using Me_3Al in CH_2Cl_2 solvent at -50° in the presence of 2,6-di-tert-butylpyridine (DtBP) and 1,8-bis(dimethylamino)-naphthalene (BDMeAN). This well-investigated model system [21] showed 90% conversion of TMP and the formation of the expected products suggesting t-butylation, proton elimination, and dimerization; however, reaction did occur in the presence of DtBP (Me_3Al/DtBP = 1). Then polymerization of styrene with the t-BuCl/Me_3Al initiating system in CH_2Cl_2 at -50°C was carried out; however, polymerization in the presence of DtBP failed to occur even when the Me_3Al concentration was raised to Me_3Al/DtBP = 10. Similar results have been obtained with 4-methyl-2,6-di-tert-butylpyridine (MeDtBP). Proton NMR spectroscopy did not show evidence for interaction between Me_3Al and DtBP. It was postulated that "H_2O" impurities are involved in the initiation process and that the hypothetical acid $H^{\oplus}Me_3AlOH^{\ominus}$ or $H^{\oplus}Me_3AlOAlMe_2OH^{\ominus}$ necessary for reaction to occur was neutralized by the hindered base. Unfortunately, these experiments had to be discontinued and were resumed only in 1977 (19).

The next series of exploratory experiments has been carried out with α-methylstyrene (αMeSt) and "H_2O"/BCl_3, "H_2O"/$SnCl_4$, "H_2O"/$AlCl_3$, etc. initiating systems using CH_2Cl_2 solvent and various sterically hindered bases, i.e., DtBP, MeDtBP, BDMeAN, and diisopropylethylamine (DiPEA). Most gratifyingly, polymerization of αMeSt readily occurred in the presence of most of the proton traps tried (a notable exception was BDMeAN). This breakthrough was rapidly followed up and a series of runs showed that, as expected, polymer yields decreased with the concentration of proton traps; however, unexpectedly, molecular weights and molecular weight dispersities ($\bar{M}_w/\bar{M}_n$) were much higher and narrower, respectively, than those of control experiments. Table 1 shows the results of a representative set of comparative experiments. At this point a commitment to investigate these discoveries in depth was made.

One of the first decisions concerned the selection of the particular system(s) for detailed investigations. Since our interest mainly concerns olefin polymerizations, we decided to start with an

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TABLE 1. α-Methylstyrene Polymerization in the Presence of Different Sterically Hindered Bases ([αMeSt] = 0.62 M, [BCl_3] = 3.0×10^{-3} M, CH_2Cl_2, -55°C, 5 min; last ingredient added was BCl_3)

Proton trap			Conversion	M_n	
Nature	pK_a[a]	$\times 10^{-3}$	(%)	$\times 10^3$	$\bar{M}_w/\bar{M}_n$
-	-	-	100	31	4.6
DtBP	3.58[b]	0.25	68	138	1.6
DtBP	3.58[b]	7.7	41	165	1.6
MeDtBP	4.41[c]	5.0	49.2	130	1.6
BDMeAN	1.6[d]	4.4	0	-	-
DiPEA	3.3[e]	5.7	35.7	82	1.6

[a]Determined in 50% aqueous ethanol.
[b]H. C. Brown and B. Kanner, J. Am. Chem. Soc., 75, 3865 (1953).
[c]E. Deutsch and N. K. V. Cheung, J. Org. Chem., 38, 1123 (1973).
[d]R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, Chem. Commun., p. 723 (1968).
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investigation of α-methylstyrene and isobutylene, representatives of an aromatic and aliphatic monomer. Most subsequent articles concern these systems; however, other monomers, e.g., styrene and indene, have also been investigated [22]. As to initiating systems, we decided to use conventional Friedel-Craft acid coinitiators in open systems, e.g., "H_2O"/BCl_3, "H_2O"/$SnCl_4$, "H_2O"/$AlCl_3$, and nonprotic cationogens in conjunction with these acids, e.g., pentamethyl benzyl chloride/$SnCl_4$. The rationale for using the latter combinations was our desire to achieve controlled cationation with conventional Friedel-Crafts halides in the presence of proton traps, a reaction which until now could be achieved only with certain alkylaluminum-based systems, e.g., cumylation by $C_6H_5C(CH_3)_2Cl/Et_2AlCl$ (see above).

Finally, scouting experiments have been run to aid the selection of the particular proton traps. Since polymerization of αMeSt did not occur in the presence of BDMeAn (see Table 1), the use of this hindered amine was ruled out. A series of experiments with DiPEA showed that premixing this amine with BCl_3 (CH_2Cl_2 solutions aged for 30 min at -50°) prevented αMeSt polymerization to occur. In contrast, DtBP under similar conditions did not affect the polymerization of αMeSt. Table 2 shows some comparative data. Evidently the lone pair of electrons of the N atom in DiPEA is not completely shielded and may slowly interact with BCl_3. This does not happen with DtBP.

TABLE 2. Polymerization of αMeSt with Proton Trap/BCl_3 Mixtures ([αMeSt] = 0.62 M, [BCl_3] = 5×10^{-3} M, CH_2Cl_2, -50°C, 5 min; premixed proton trap-BCl_3 mixtures added last)

Proton trap	Proton trap/BCl_3	Conversion (%)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
DtBP	1.5	41.2	110	1.6
DiPEA	1.5	0	-	-

Inspection of pK_a values in Table 1 indicates that high basicity is a necessary but not sufficient requirement for efficient proton trapping in cationic polymerizations. Other experiments have indicated that alkylation of the open 4-position of DtBP does not occur under polymerization conditions and that for all practical purposes MeDtBP and DtBP behave identically. On the basis of these experiments and observations, it was decided to employ DtBP in our future detailed investigations.

Note Added in Proof. We are pleased to note that after our preliminary presentations on this subject [23-25], a team of French investigators has recently used a sterically hindered pyridine MeDtBP in elucidating the mechanism of carbocationic polymerizations [26].

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