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Kinetically Controlled Regioselective Formation of a Tail-to-Tail Dimer Dianion of 4-(*N*,*N*-Dimethylamino)styrene

William N. Warner and Thieo E. Hogen-Esch*

Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089

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Introduction. Poly(aminostyrenes) (PAM's) are potentially versatile polymers.[1−8] The presence of the amine functionality allows the formation of hydrophilic polymers through quaternization or protonation,[2] the introduction of chromophores[1c] or other functional groups, the formation of metal complexes,[3] and the convenient formation of graft copolymers.[4] Because of the acidity of primary or secondary amino groups relative to benzylic anions, only anionic polymerizations of the PAM's with tertiary or protected amino groups are possible. The living anionic polymerization of DMAS has been reported.[6,7]

Here we report what appears to be the first *kinetically* controlled and regioselective tail-to-tail dimerization of 4-(*N*,*N*-dimethylamino)styrene (DMAS) in the presence of a large excess potassium metal to give the corresponding 1,4-dipotassio-1,4-bis(4′-(*N*,*N*-dimethylamino)phenyl)butane in quantitative yield. This dimer anion is capable of initiation of styrene, thus providing PDMAS−polystyrene (PS−PDMAS−PS) "block" copolymers having a well-defined central 1,4-bis(4′-(*N*,*N*-dimethylamino)phenyl)butylidene group.

Results and Discussion. a. Polymerizations. The synthesis of DMAS through reaction of DMAB with methylidenetriphenylphosphorane (see Experimental Section) gave DMAS in excellent (91%) isolated yield compared with previous methods.[7] However, removal of residual DMAB by reduction with $NaBH_4$ was needed to obtain DMAS that was sufficiently pure. Thus, DMAS that was purified by vacuum distillations (2 times) from calcium hydride without treatment with $NaBH_4$ gave a wide MW distribution and a poor agreement of calculated and determined molecular weights (MW's) (Table 1, run 1).

Table 1. Polymerization of DMAS Initiated with *t*-BuLi in THF at −78 °C[a]

run	time (h)	conv (%)[b]	M_n (calc)[c]	M_n (NMR)[d]	M_n (SEC)[e]	PDI
1[f]	10	50	4100	47000	48400	1.57
2	12	>95	12500	12900	13000	1.13
3	12	>95	10700	11000	11000	1.15
4	5	45	2700	2700	2800	1.09
5	0.5	2		350	380	1.06
6[g]	16	65		300	310	1.01

[a] [DMAS] = 0.4 M, [*t*-BuLi] = about 4 mM, THF = 25 mL. [b] Percent conversion, determined gravimetrically. [c] M_n(calc) = [DMAS](converted)/[*t*-BuLi]. [d] Determined by NMR; see text. [e] By SEC using PS standards. [f] DMAS not treated with $NaBH_4$. [g] DMAS was stirred over excess K metal in THF at −78 °C for 12 h.

Several *t*-BuLi initiated polymerizations at −78 °C were carried out by slow addition of DMAS either in bulk or as a 1.0 M THF solution to the initiator solution using reported methods.[6,7] Rapid initiation occurred as seen by the immediate onset of the brownish red color of the benzylic anion, but propagation was extremely slow, with less than monomer conversion after 30 min, and compete polymerization under the reaction conditions of Table 1 required about 12 h, in agreement with a previous report.[7] MW distributions were narrow, and there was good agreement between the number-average MW's calculated and determined by *both* SEC and NMR the latter through integration of the *tert*-butyl (0.65 ppm) and dimethylamino protons (2.90 ppm), confirming that the polymerizations were living (Table 1, runs 2−5).[7]

b. Dimerization of DMAS. We next turned our attention to the electron transfer initiated polymerizations.[8] Upon stirring DMAS (150 mg, 1.0 mmol) dissolved in 25 mL of THF at −78 °C in the presence of a large excess (4.0 g, 10 mmol) of potassium mirror for 12 h followed by filtration and reaction of the filtered carbanion solution with methanol, the pure 1,4-bis(4′-

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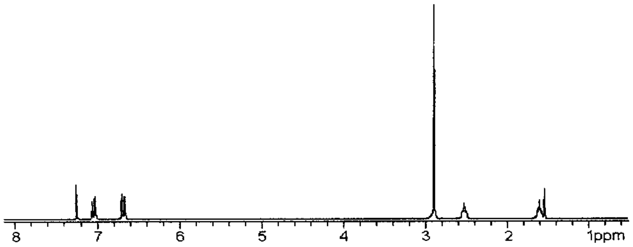


Figure 1. Proton NMR spectrum of the dimer of DMAS in $CDCl_3$ at 25 °C.

Table 2. Effect of K Metal Mass on Dimer Dianion Formation in THF at −78 °C[a]

run	K metal (g)[b]	K metal (mmol)[b]	conv (%)[c]	M_n(SEC)	PDI
1	0.4	10	50	5400	1.31
2	0.8	20	90	3000	1.19
3	1.0	25	>95	1200	1.11
4	2.0	50	>95	500	1.35
5	4.0	100	>95	290	1.01
6[e]	4.0	100	>95	310	1.01

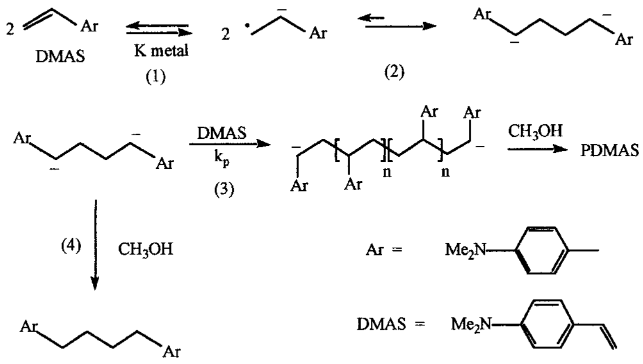
[a] DMAS = 150 mg (1.0 mmol), THF = 25 mL, reaction time = 30 min. [b] Amount of K metal used to make the metal mirror. [c] Percent DMAS conversion, determined gravimetrically. [d] Determined by cutting/weighing of the SEC peaks of Figure 2. [e] See run 6, Table 1.

(*N*,*N*-dimethylamino)phenyl) butane—the tail-to-tail dimer—was formed in *quantitative yield*. The structure of the dimer is clearly identified by two methylene resonances of equal magnitude at 2.55 and 1.60 ppm that are both multiplets as a result of non-first-order [9c] interactions (Figure 1). The resonance at 1.48 ppm is due to a solvent impurity. Note the absence of asymmetric centers, the presence of which would greatly complicate the spectrum.[9] For instance, the trimer formed by addition of a single monomer to the dianion prior to protonation would give rise to *three* different methylene groups with the two protons in each methylene group being diastereotopic due to the presence of a single asymmetric center. The tetramer spectrum would be even more complicated due to the formation of configurational isomers. The exclusive presence of the dimer is also consistent with a *single* low monodisperse MW SEC peak at an elution volume of 22.7 mL (not shown) and the absence of residual monomer verified by both NMR and SEC. Mass spectral analysis confirmed the dimer structure (parent peak at 296 Da).

Oligomerizations carried out at −78 °C for about 1.5 h with potassium mirrors containing less metal gave increasing amounts of higher oligomers (Table 2, runs 1−4). This indicates that the electron transfer to DMAS (Scheme 1, eq 1) is the rate-determining step in the formation of dimer as the dimerization of radical anions (eq 2) is known to be very rapid.[10,11] Thus, for the case of lithium metal (chunks) the initiation reaction leads to the formation of dimers and higher oligomers consistent with the smaller metal surface (Table 2, run 4).

Apparently in the present case, the electron transfer and subsequent dimerization of the radical anion occur quickly enough to consume *all* of the monomer that is polymerized slowly compared to electron transfer to DMAS and dimerization. For instance, the reported[7] polymerization rate constant of DMAS in THF at 25 °C in the presence of potassium ion is roughly 3 orders of magnitude smaller than that of styrene under the same conditions—a result that we have confirmed.[12] We have also determined the DMAS polymerization rate constant in THF at 25 °C in the presence of Li ion[12] to have a value of about 1.0 M^{-1} s^{-1}, about 160 times slower than the rate constant for the polymerization of styrene under the same conditions.[13,14]

Scheme 1. Formation of Tail-to-Tail DMAS Dimer in the Presence of Alkali Metals



The above DMAS dimerization appears to be the first instance of a *kinetically* controlled radical anion-mediated dimerization. The apparently unprecedented exclusive formation of the DMAS dimer dianion under the above conditions is surprising given the nature of living polymerizations.[10] Stereoselective radical anion-mediated vinyl monomer dimerization has only been reported for the case of sterically hindered α-substituted vinylaromatic monomers such as 1,1-diphenylethylene,[11] 3-methyl-2-phenyl-1-butene (MPB),[15] and similar vinyl monomers, the polymerization of which is thermodynamically inaccessible.

The slow rate of anionic polymerization of DMAS relative to styrene is expected to be due, at least in part, to the greater electron density at the monomer methylene carbon due to the presence of the electron-donating dimethylamino group in the para position. This is supported by an approximately 5 ppm carbon-13 NMR upfield shift of the DMAS β methylene carbon compared to that in styrene.[12]

A large decrease in the polymerization rate constant relative to styrene (factor of about 20) has been demonstrated for the polymerization *p*-methoxystyrene (PMS) in THF at 25 °C in the presence of Na ion.[16] Although other factors such as ion pair dissociation and or solvation involved in anionic polymerizations are likely to be important as well,[17] the increased electron density at the β methylene group of the monomer may have played a similar role there also.

DMAS Dimer Dianion Initiated Polymerizations of Styrene. The $DMAS_2$ dianion prepared under the above conditions (large excess of potassium metal mirrors) was also used as an initiator for the polymerization of styrene. Interestingly, the initiation of styrene by addition of styrene/THF solutions to carefully filtered solutions of the DMAS dimer dianion potassium salt was extremely *rapid*, as seen by the immediate onset of the bright red color of polystyrylpotassium upon allowing styrene vapor to contact the DMAS dianion. Narrow MW distribution PS-*b*-$DMAS_2$-*b*-PS "block" copolymers having the DMAS dimer at the center are obtained in this case. There was excellent agreement of the M_n values determined by proton NMR—obtained by integration of the dimethylamino groups of the DMAS dimer and the methylene/methine PS protons—with that obtained by SEC and that calculated from the styrene/DMAS dimer ratio, assuming complete DMAS conversion to the dianion. For example, using the conditions shown in Table 1, the number-average MW's obtained by NMR, SEC, and that calculated were found to be 16 600, 16 900, and 16 500, respectively, and the SEC MW distribution was 1.08.

The successful initiation/polymerization of other monomers such as dienes and other monomers that are readily initiated by PS anions is expected. Quaternization of such precursors with polymers having reactive halogen or similar end groups is expected to give hetero-four-arm star polymers.[4a,18]

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