

## Effects of Aging on Some Anionic Initiators

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### Synopsis

The effects of aging on sodium naphthalene and sodium  $\alpha$ -methylstyrene initiators, prepared in 1957, were investigated. The green sodium naphthalene had turned brown and faded; the aged sample failed to initiate the polymerization of  $\alpha$ -methylstyrene at low temperature. Naphthalene had been completely converted into dihydronaphthalene; the retention of the brown color reflected a relative stability of anions of the latter. The freshly prepared brown sodium-dihydronaphthalene complex was also ineffective for polymerization of  $\alpha$ -methylstyrene. No evidence for the cleavage of the ether solvent (tetrahydrofuran) on aging was obtained. The aged sodium  $\alpha$ -methylstyrene initiator retained its vivid red color and effectiveness in the polymerization of  $\alpha$ -methylstyrene. The inherent better stability of dianions than of radical anions was thus confirmed. Since the sodium  $\alpha$ -methylstyrene initiator was actually a low molecular weight "living" polymer, the 7-yr. aging test demonstrated, in effect, the "longevity" of living polymers. The structure of the "living tetramer" of  $\alpha$ -methylstyrene was discussed in the light of previous studies and present results. Apparent discrepancies were pointed out, and the necessity of more comprehensive studies was indicated.

### Introduction

Under suitable experimental conditions, the anionic polymerization initiated by an electron transfer and involving no termination<sup>1</sup> yields well defined, nearly monodisperse polymers. These suitable conditions include the rigorous purity of reactants. The solutions of initiators used are particularly prone to contain undesirable impurities. The initiators are prepared beforehand, usually distributed into ampules and often stored for some time prior to use. Hence, the impurities initially present may be augmented during aging by products of side reactions. The difficulties can be largely avoided or minimized by using freshly prepared initiators whenever practical. Nonetheless, knowledge of the effects of aging on initiators and of their relative stability is of considerable importance.

Some unused initiator solutions, which had been prepared by the writer in 1957 in the laboratories of Prof. Szwarc at Syracuse, happened to be available. This circumstance offered a unique opportunity for examining the final effect of 7-year aging. The initiators were the conventional sodium naphthalene (Na-Naph) and the "living tetramer" of  $\alpha$ -methylstyrene (Na- $\alpha$ -MS), both in tetrahydrofuran (THF). Originally these initiators were of good quality, since other ampules from the same batches gave accurate and consistent results in the early studies.<sup>2</sup> During the long

storage, the initiator ampules remained in a box, i.e., in darkness, and did not experience any extremes of temperature. Only small volumes of the aged initiator solutions were available and the original strengths were no longer known. The tests that followed were limited and mainly of a qualitative nature. The general behavior of Na-Naph on aging, i.e., gradual conversion of naphthalene into dihydronaphthalene, was known both from the literature<sup>3</sup> and from experience. The Na- $\alpha$ -MS initiator was of greater interest. This initiator is actually a low molecular weight "living" polymer. Hence, its stability would, in effect, provide a criterion for the "longevity" of living polymers.

### Results

Visual inspection of the ampules with aged initiator solutions, and comparison with freshly prepared control samples, was revealing. The old Na-Naph initiator solutions had changed color and faded. Whereas the fresh initiator was green, the aged samples ranged from dark brown to practically colorless. An interesting correlation of the color intensity with the volume of liquid in ampule was noted (the ampules originally had uneven amounts of catalyst solution, but the lengths of tubing sealed under vacuum were approximately the same). The ampule with the least amount of liquid was dark brown; the ampule with a large volume of liquid was nearly colorless; and the one with intermediate amount was light brown. These ampules contained solutions from the same batch, hence initially had the same concentrations. In contrast, the old Na- $\alpha$ -MS initiator solutions had retained their vivid red color. This color was somewhat less intense than in the fresh control samples. No definite significance could be attached to this difference of intensity since the exact original concentration was unknown.

The retention of ability to initiate polymerization was tested qualitatively by adding the old initiators to THF solutions of  $\alpha$ -methylstyrene ( $\alpha$ -MS) at  $-30^{\circ}\text{C}$ ., i.e., well below the ceiling temperature for the monomer. This critical test involved small quantities and was essentially of the positive-negative character. The aged Na- $\alpha$ -MS initiator proved effective in producing a high molecular weight polymer. On addition to  $\alpha$ -MS, the red color persisted, the solution became more viscous, and a copious precipitate was obtained on pouring this ethereal solution into methanol; the yield was quantitative. In contrast, the darkest, presumably the most potent, aged Na-Naph sample failed to initiate the polymerization.

The brown color of the aged Na-Naph solutions was apparently caused by the presence of anions of the expected dihydronaphthalene.<sup>3</sup> It was of interest, therefore, to test in an independent experiment the initiation effectiveness of sodium dihydronaphthalene (Na-DHN). The Na-DHN complex was prepared by the procedure identical with that used in preparation of Na-Naph. The brown Na-DHN solution was then used in the polymerization test described. No vivid red color characteristic of methylstyryl anions developed, the solution fading to a milky yellow one. On

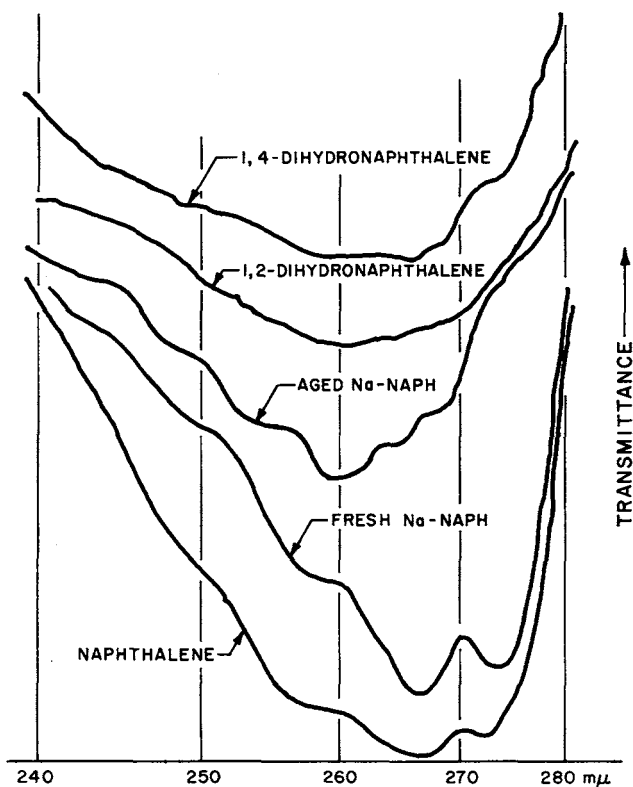


Fig. 1. Ultraviolet spectra.

precipitation in methanol, a small amount of a white powder was obtained. The infrared spectrum showed that only the initiator was recovered (separately precipitated Na-DHN also gave a white powder with an identical spectrum).

When the contents of the ampules were exposed to air, the original colors disappeared, and a gradual yellowing, particularly in the case of the old Na- $\alpha$ -MS, was observed. A white flocculant precipitate appeared in the aged Na- $\alpha$ -MS ampule. The old Na-Naph solution also left a waxy deposit when the volume of solvent decreased somewhat by evaporation.

An interaction of the aryl component with the ether solvent during storage would be expected to produce new solvent fractions. The separation was attempted by chromatography on freshly opened samples. Both the fresh and the aged solutions of Na-Naph and Na- $\alpha$ -MS gave only one peak, corresponding to THF in a control experiment. This result indicated that no cleavage of ether had occurred on storage. The Na- $\alpha$ -MS solutions gave no peak corresponding to monomeric  $\alpha$ -MS. Failure to detect monomeric  $\alpha$ -MS in the aged Na- $\alpha$ -MS sample indicated that no degradation of the initial tetramer to the monomer level had taken place. Furthermore, no other related simple compounds having boiling points near that

of  $\alpha$ -MS were present (b. p.:  $\alpha$ -methylstyrene 165°C., styrene 145°C., cumene 152.4°C.). The chromatographic results do not preclude the possibility of interactions leading to higher molecular weight products.

The subsequent spectroscopic tests were carried out on the contents of open ampules of depleted initiators. It is realized that the results are less

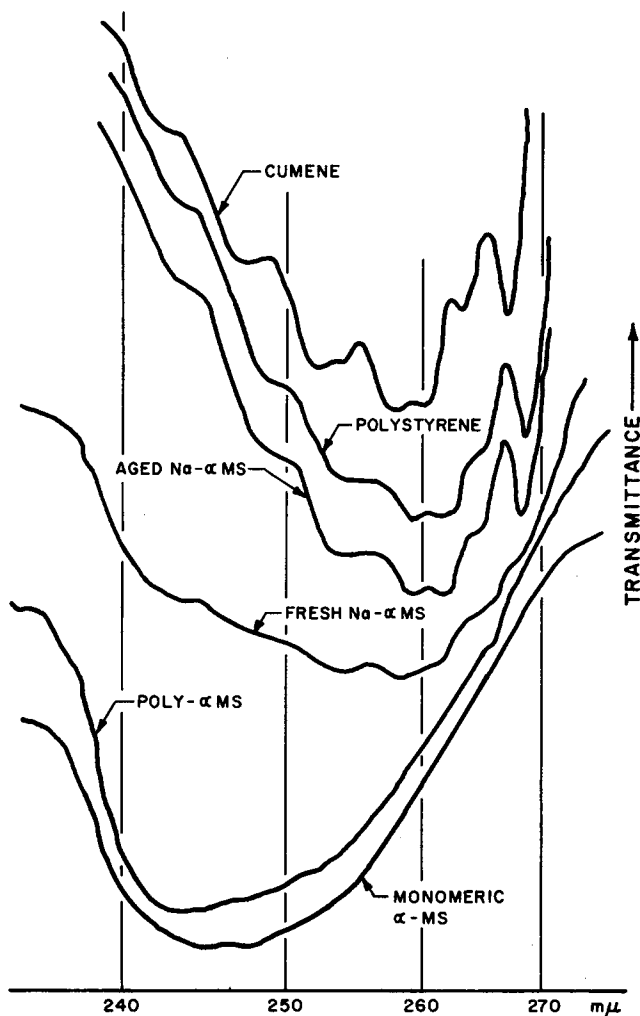


Fig. 2. Ultraviolet spectra.

reliable, since the effects of aging were probably compounded with the effects of post-reactions (involving air, moisture, and residual sodium). Nonetheless, the fresh and the aged solutions still could be compared, and the nature of the immediate precursors of the final products could be tentatively inferred.

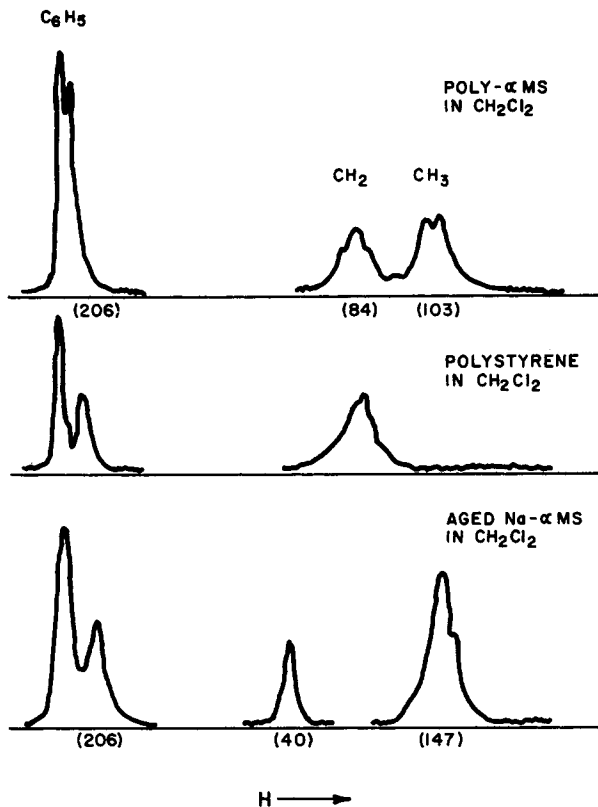


Fig. 3. NMR spectra.

No differences in the infrared absorption peaks associated with THF solvent were observed in the fresh and the aged solutions, thus corroborating the chromatographic results that THF did not cleave or degrade. When comparing the infrared spectra of the fresh and the aged Na-Naph (smears), the most pronounced differences observed were in the region of 12–15  $\mu$ , i.e., out-of-plane bending vibrations of aromatic C—H bonds. There was no indication of any naphthalene (peak at 12.8  $\mu$  in the control solution of naphthalene and in the fresh Na-Naph) remaining in the aged Na-Naph. The spectrum of the aged Na-Naph (peaks at 13.1 and 14.3  $\mu$ ) indicated the conversion had proceeded further than to the stage of dihydronaphthalene. The infrared spectra of the fresh and the aged Na- $\alpha$ -MS were virtually identical.

The ultraviolet spectrum of the aged Na-Naph showed general semblance to that of dihydronaphthalene, although in the former the broad peak was shifted more to shorter wavelengths (Fig. 1). The ultraviolet spectra of Na- $\alpha$ -MS initiators (Fig. 2) exhibited greater divergence than their infrared spectra. The monomeric  $\alpha$ -MS and the anionically initiated poly- $\alpha$ -MS showed absorption peaks at about 242  $m\mu$ , the aged Na- $\alpha$ -MS gave a

differently shaped curve with a peak at 260  $m\mu$ , and the relatively fresh Na- $\alpha$ -MS exhibited a curve of intermediate shape. The ultraviolet curve of the aged Na- $\alpha$ -MS resembled those of polystyrene and of cumene. To distinguish between these alternatives, the NMR approach was adopted. It was hoped comparison of the ratios of signals due to methyl and phenyl protons would be illuminating.

The NMR spectra are shown in Figure 3; normalized areas of peaks, in arbitrary units, are given in brackets. The NMR spectrum of anionically initiated poly- $\alpha$ -MS is practically identical with that obtained by Sakurada et al.<sup>4</sup> on the sodium-initiated polymer (sample NM-1-1). The spectrum of the aged Na- $\alpha$ -MS showed an increase of methyl groups by a factor of 147/103, i.e., 1.42, thus being decidedly in favor of cumenelike structure.

### Experimental

The original initiators had been prepared in 1957 by the then employed, and now conventional, methods involving the use of high vacuum, break-seals, and constrictions instead of stopcocks.<sup>2,5</sup> The fresh initiators were prepared by the identical experimental procedure. Thus, the Na-Naph initiator was prepared by admitting a THF solution of naphthalene onto a sodium mirror, allowing them to react, filtering the resultant deep-green solution through a fritted glass disk into a side flask, sealing off at the constriction, and finally distributing into breakseal ampules. The above procedure was used for Na-DHN (DHN from Aldrich Chemical Co., 1,2-isomer, tech. grade, middle fraction); the chocolate-brown solution developed immediately upon contact of the DHN with the sodium mirror. The Na- $\alpha$ -MS initiator was obtained in a similar way by contacting the approximately 0.5 M solution of  $\alpha$ -MS with a sodium mirror at room temperature. The resultant ruby-red solution contained tetrameric dianions, as demonstrated earlier ebullioscopically and by titration of the derived dicarboxylic acid.<sup>2,6</sup>

The chromatographic separation was attempted on a column packed with Fluoropak 80 (91%), D. C. 550 phenylmethylsilicone oil (7%) and Carbowax 400 (2%). At 110°C. in a control experiment, the retention time for THF was 1.4 min, and that for monomeric  $\alpha$ -MS, 16.5 min.

The infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer using sodium chloride optics. First, the spectra were taken of THF solutions, and then of smears, i.e., by depositing a few drops of THF solution on NaCl disk and allowing the solvent to evaporate. The ultraviolet spectra were obtained on a Beckman DK-2 ratio recording spectrophotometer (THF solution versus pure THF). The NMR spectra were taken on a Varian HR 60 spectrometer. After trying several solvents, methylene dichloride was found the most satisfactory.

### Discussion

The literature contains numerous observations on the deleterious effects of aging on an initiator performance in anionic polymerization. A few

experiments, like that of Wenger,<sup>7</sup> involved an intentional use of old catalysts. The aging time was usually limited to several weeks, or months at the most. The aging time in the present work is of the different order of magnitude (by circumstance rather than intent). In the absence of periodic checks, this fact would not appear to be of any particular significance. Indeed, in the case of Na-Naph, the main changes had probably occurred in the early period of storage. However, the long-aged samples, particularly Na- $\alpha$ -MS, provided some unique results.

The Na-Naph initiator underwent a complete change on aging. As expected, naphthalene had been converted into dihydronaphthalene, following the mechanism proposed early by Paul, Lipkin, and Weissman.<sup>3</sup> Further changes, presumably involving the nonaromatic double bond, could have occurred later in post-reactions. An interesting fact was that the brown color of DHN anions was preserved. This retention of color and the ease of formation of a chocolate-brown solution on contacting DHN with a sodium mirror, reflected the relative stability of Na-DHN.

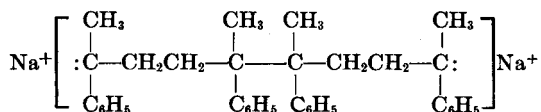
Baer<sup>8</sup> thought that Na-DHN would be insufficiently basic to initiate the polymerization of styrene, and that the observed discrepancy between the actual efficiency of Na-Naph and the efficiency expected from the titration for total basicity was due to the presence of some Na-DHN even in relatively fresh Na-Naph. On the other hand, the results of Hartley<sup>9</sup> implied the Na-DHN could be effective at least in the initiation of polymerization of methyl methacrylate (MMA). Hartley found evidence of the presence of dihydronaphthalene bonded to MMA when the latter was polymerized with the use of an aged Na-Naph initiator. Previously, Tobolsky and Hartley<sup>10</sup> established that the fresh Na-Naph initiated the polymerization of MMA by an electron transfer. Perhaps the Na-DHN is effective only with more reactive monomers; in the case of acrylonitrile the Na-DHN might even prove more suitable than the potent Na-Naph. However, the present work demonstrated the Na-DHN was ineffective in the attempted polymerization of  $\alpha$ -MS at low temperature.

Brower and McCormick<sup>11</sup> obtained evidence for the cleavage of the ether solvent (ethylene glycol dimethyl ether) after 3-week initiator aging. In contrast, no evidence for such a cleavage was obtained in the present work. This fact indicates the preference of THF over ethylene glycol dimethyl ether as a solvent. Apparent noninteraction of the catalyst with the solvent makes it more difficult, however, to interpret the observed correlation of the extent of deterioration of Na-Naph (or rather Na-DHN) with the volume of liquid in ampules. Some slowly acting impurities, mentioned by Wenger,<sup>12</sup> or an autocatalytic process, might have been involved. The possibility that the THF ring did open and a further reaction ensued, leading to adducts or higher molecular weight products, cannot be entirely excluded. The matter remains open to speculation.

The Na- $\alpha$ -MS was actually a "living" oligomer of  $\alpha$ -MS. The present investigation found this initiator remarkably stable, as evidenced by retention of the red color and of the initiation-effectiveness after 7-yr. storage.

This test of "longevity" vindicated the term "living polymers." It also demonstrated better inherent stability of dianions than that of radical anions. The practical implication is that the Na- $\alpha$ -MS initiator is well suited for polymerizations involving time delay, and that the determination of its strength by titration for basicity should be quite reliable. The Na- $\alpha$ -MS certainly deserves closer attention.

Rembaum and Szwarc<sup>13</sup> noted that tetramers were formed in the reaction of  $\alpha$ -MS with Na-Naph at room temperature. Shortly afterward, the writer<sup>2,14</sup> obtained the tetramer by the direct interaction of  $\alpha$ -MS with a sodium mirror, and demonstrated the usefulness of this living tetramer of  $\alpha$ -MS as an initiator which avoids the pitfalls of the presence of dihydronaphthalene. Apparently, the work at The Dow Chemical Co.<sup>11</sup> followed the same lines. Actually, the idea of using a low molecular weight polymer as an initiator was not new; it was applied, for instance, by Ballard and Bamford<sup>15</sup> in 1954 in the polymerization of *N*-carboanhydrides. Richards and Szwarc<sup>16</sup> used this Na- $\alpha$ -MS initiator early in the study of the copolymerization of styrene with ethylene oxide. Later, Wenger<sup>12</sup> also prepared the Na- $\alpha$ -MS by the sodium mirror method and extensively studied the application of Na- $\alpha$ -MS as an initiator and as a purging agent. Wenger,<sup>7</sup> however, maintained that actually the whole gamut of oligomeric dianions, predominantly dimers, was involved in the initiation step. Indeed, Frank et al.,<sup>17</sup> by the isolation of 2,5-dimethyl-2,5-diphenyladipic acid upon the reaction of  $\alpha$ -MS with sodium dispersion in ethylene glycol diethyl ether (and subsequent carboxylation), demonstrated that dimers were formed under their experimental conditions. Subsequently, Szwarc and co-workers<sup>6,18,19</sup> extensively studied the conditions of formation and relative stabilities of the oligomers of  $\alpha$ -MS. It was confirmed<sup>18</sup> the most stable species is the tetramer, obtainable by the sodium mirror technique. To this stable tetramer was assigned the head-to-head central configuration, arising from the coupling of two tail-to-tail radical-anion dimers:



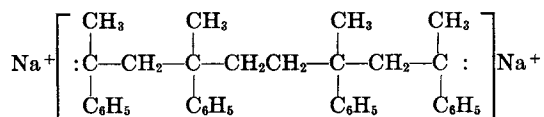
Other species, including a dimer (obtainable by the sodium dispersion method), were found subject to easy degradation.

There is no doubt the Na- $\alpha$ -MS used in the present investigation was initially in the tetrameric state.<sup>2</sup> However, it is not certain this tetramer was really so stable. Spectroscopic results showed the aged Na- $\alpha$ -MS either had suffered changes on storage or exhibited greater vulnerability to post-reactions than did the fresh initiator. Also, the spectroscopic results, particularly the NMR, confused the picture of the structural configuration of tetramer. It is hard to visualize the formation of cumenelike species, i.e., the increase of methyl groups, from a tetramer with head-to-head central configuration. The extra methyl groups could have arisen only



from terminal methylenic groups. An unlikely split of the end mers should have been evidenced by the presence of either monomeric  $\alpha$ -MS or cumene in the chromatographic separation.

The NMR results could be rationalized more easily if it were assumed that, at some stage, the precursor of the final product was a tetramer with a tail-to-tail central structure:



For then, central rupture into dimers (probably followed by a  $\beta$ -hydrogen shift) would eventually result in the increase of methyl groups by a factor of 3/2, i.e., 1.50, as compared with the observed factor of 1.42. For the purpose of this argument, it is irrelevant whether such a rupture occurred during storage or in post-reactions.

This scheme, however, does not avoid all difficulties. It is unlikely the required precursor, a tetramer with a tail-to-tail central configuration, could be formed by the coupling of two head-to-tail radical-anion dimers, as suggested by Wenger,<sup>12</sup> since the isolation of substituted adipic acid by Frank<sup>17</sup> indicates the preference of dimers for the tail-to-tail linkage. The rearrangement of the tetramer during storage is unlikely. One possibility is the initial formation of the tail-to-tail dimer followed by addition of one mer to each end. Another possibility is the growth of the original tetramer to higher oligomers during storage, followed later by splitting at methylenic linkages.

The above speculations are based mainly on indirect and limited evidence. They are primarily intended to stimulate the deserved interest in the Na- $\alpha$ -MS initiator, and to provoke re-interpretations and supporting studies. The writer was prevented from further experimentation in this area by the scope of his principal work. Verification and further studies leading to broader evidence and firmer conclusions are clearly desirable.

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### Résumé

On a étudié les effets du vieillissement sur du sodium naphthalène et sur du sodium- $\alpha$ -méthylstyrène, qui avaient été préparés en 1957. Le sodium naphthalène vert s'est décoloré en brun et cet échantillon vieilli n'initiait plus la polymérisation de l' $\alpha$ -méthylstyrène à basse température. Le naphthalène s'est complètement transformé en dihydronaphthalène et la rétention de la coloration brune constitue un indice de la stabilité relative des anions issus de ce produit. Le complexe brun sodium-dihydronaphthalène fraîchement préparé est également inefficace pour polymériser l' $\alpha$ -méthylstyrène. Il ne semble pas s'être produit de réaction d'ouverture du solvant éthéré (tétrahydrofurane) lors du vieillissement. L'initiateur sodium- $\alpha$ -méthylstyrène vieilli conserve sa couleur rouge vif ainsi que son efficacité dans la polymérisation de l' $\alpha$ -méthylstyrène. Ceci confirme donc que la stabilité inhérente aux di-anions est supérieure à celle des radicaux anions. Puisque l'initiateur sodium- $\alpha$ -méthylstyrène est en fait un polymère vivant de bas poids moléculaire, les tests de vieillissement effectués après 7 ans ont démontré la longévité des polymères vivants. La structure du tétramère vivant d' $\alpha$ -méthylstyrène a été discutée à la lumière de la présente étude et des données déjà connues. On a mis l'accent sur quelques points de désaccord ainsi que sur la nécessité d'une étude plus approfondie.

### Zusammenfassung

Der Einfluss der Alterung auf 1957 hergestellte Natrium-Naphthalin- und  $\alpha$ -Methylstyrol-Natrium-Startersysteme wurde untersucht. Das grüne Natrium-Naphthalin hatte sich braun verfärbt und war ausgeblasst; die gealterte Probe lieferte keine Anregung der Polymerisation von  $\alpha$ -Methylstyrol bei tiefer Temperatur. Das Naphthalin war völlig in Dihydronaphthalin umgewandelt; die Beständigkeit der braunen Farbe lies die relative Stabilität der Anionen letzterer Verbindung erkennen. Ein frisch hergestellter Dihydronaphthalin-Komplex war für die Polymerisation von  $\alpha$ -Methylstyrol ebenfalls unwirksam. Es wurden keine Hinweise für eine Spaltung des Äther-Lösungsmittels (Tetrahydrofuran) bei der Alterung erhalten. Das gealterte  $\alpha$ -Methylstyrol-Natrium-Startersystem behielt seine lebhafte rote Farbe und seine Wirksamkeit bei der Polymerisation von  $\alpha$ -Methylstyrol bei. Die spezifische bessere Stabilität von Dianionen gegenüber Radikalanionen wurde somit bestätigt. Da das  $\alpha$ -Methylstyrol-Natrium-Startersystem tatsächlich ein niedermolekulares "lebendes" Polymeres enthält, zeigte der 7-Jahr-Alterungstest effektiv die "Langlebigkeit" von lebenden Polymeren. Die Struktur des "lebenden Tetrameren" von  $\alpha$ -Methylstyrol wurde im Lichte früherer Untersuchungen und der gegenwärtigen Ergebnisse diskutiert. Offensichtliche Widersprüche wurden festgestellt und die Notwendigkeit einer umfassenderen Untersuchung betont.

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