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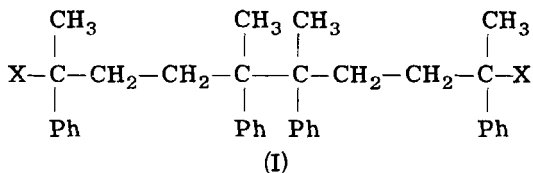
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LETTER TO THE EDITOR

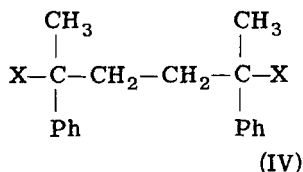
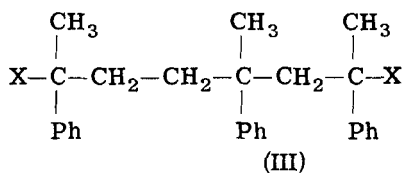
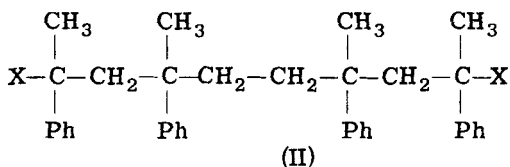
## A Remark to the Termination Reaction of Living $\alpha$ -Methylstyrene by Methanol

The tetrameric dianion



with  $\text{X} = \ominus$  was claimed to be the most stable thermodynamic living oligomer of  $\alpha$ -methylstyrene in the depolymerization of living poly( $\alpha$ -methylstyrene) [1]. The formulation of structure (I) was supported by thermodynamic considerations and molecular weight determinations after killing the dianion by water ( $\text{X} = \text{H}$ ) or carbon dioxide/water ( $\text{X} = \text{COOH}$ ).

Recently this structure has been questioned on the basis of nuclear magnetic resonance studies and mass spectroscopy [2]. Evidence was put forward for a tetramer structure (II) with  $\text{X} = \text{H}$ . In addition, both a trimer (III) and a dimer (IV) were isolated, all with  $\text{X} = \text{H}$ .



We have carried out similar experiments with a slight excess of monomer as calculated for tetramer formation and using methanol instead of water as a killing agent. The results of our NMR and mass-spectroscopy measurements with a product tested for its purity by thin-layer chromatography may be summarized as follows:

1. The ratio of the numbers of aromatic protons to aliphatic protons is 20.0 : 25.9 instead of 20.0 : 22.0, the latter being the ratio for a tetramer with X = H end groups. The polymer must thus contain CH<sub>3</sub> end groups.

2. In mass spectrometry, peaks at  $m/e = 474, 356,$  and  $238$  were found, confirming the existence of tetramer, trimer, and dimer all with X = H.

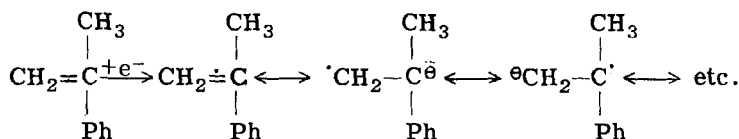
3. Another peak with  $m/e = 366$  could be due to the existence of an addition product of the dimeric anion to the naphthalene radical anion (V), resulting in a dianion which is terminated by two protons ( $m = 128 + 2 \cdot 118 + 2 \cdot 1$ ).

4. Peaks with  $m/e = 384$  and  $266$  (and  $267$  and  $265$ ) must be assigned to trimers (VII) and dimers (VI) with two methyl end groups each. No peak with  $m/e = 502$  corresponding to a tetramer with two methyl end groups could be found, however.

5. There were no peaks with  $m/e = 488, 370,$  and  $252$ , which are the mass/electron ratios for tetramers, trimers, and dimers having one methyl and one hydrogen end group each.

6. In contrast to the results of Williams and Richards [2], neither fragmentation products with peaks at  $m/e = 251$  from trimer and  $131$  from tetramer nor metastable peaks at  $267$  and  $159$  were found. The mass spectrogram showed, however, stable peaks at  $159$  and  $267$ . This discrepancy may be due to different fragmentation conditions and/or the lower concentrations of the trimer and tetramer in our mixture. Furthermore, we observed a peak at  $m/e = 277$  which cannot be explained as yet.

For the explanation of the existence of oligomers with methyl end groups it is necessary to remember that in the  $\alpha$ -methylstyrene radical anion odd electron and electron pairs are not truly separated [3]:



In the mixture, monomer M, naphthalene radical anion  $\cdot \text{Np}^\ominus$ , monomeric pseudoradical anion  $\cdot \text{M}^\ominus$ , and higher species are present. Our experiments cannot, of course, decide whether these species are in

equilibrium or the reaction is kinetically controlled. From product analysis, the following initiation and propagation steps can be envisaged (Fig. 1).

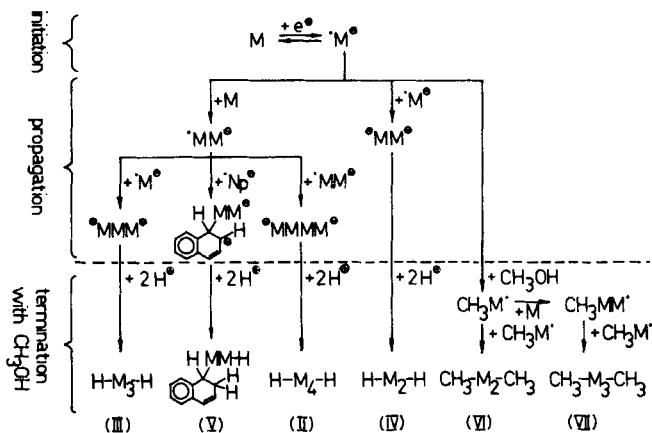


Fig. 1

By adding methanol to the mixture, all dianions are killed by the protons coming from the methanol. Tetramers, trimers, and dimers as well as the naphthalene/dimer addition product with two hydrogen end groups each are thus formed. The monomeric radical anion evidently does not react with protons. It may, however, react with methanol ( $M^\ominus + CH_3OH \rightarrow CH_3M^\ominus + HO^\ominus$ ) to give a methyl-terminated monomer radical which recombines with another methyl-terminated radical to give the dimethyl-terminated radical found. Before undergoing recombination, it may, however, add a monomer molecule to give the methyl-terminated dimer  $CH_3MM^\bullet$ , which then adds  $CH_3M^\bullet$  to form the observed dimethyl-terminated trimer. A tetramer with two methyl end groups is unlikely to be formed because of the low concentrations of these species. The postulated scheme explains furthermore why no tetramers, trimers, and dimers with mixed end groups have been observed.

### EXPERIMENTAL

A solution of 13.56 g of naphthalene and 2.43 g of sodium (0.106 mole) in 2.43 ml of tetrahydrofuran was added to 25 g of  $\alpha$ -methylstyrene (0.233 mole) in 280 ml of tetrahydrofuran at 25°C. The whole mixture was brought to  $-78^\circ C$ . After keeping it for 2 hr at this temperature, the mixture was heated 6 hr at 62°C and then 2 ml of methanol was added. Tetrahydrofuran was distilled off, the re-

maining product dissolved in 500 ml of benzene, the resulting solution washed six times with a total of 800 ml of water, and finally the benzene layer treated with activated charcoal and refluxed to get a colorless solution. Benzene, along with a large quantity of naphthalene, was removed from this solution with a rotational evaporator. An additional quantity of naphthalene was removed by sublimation under vacuum. The 29 g of product thus obtained still contained some naphthalene. The product was dissolved in petrol ether in different proportions and chilled to  $-28^{\circ}\text{C}$  to remove most of the naphthalene by way of repeated fractional crystallization. After evaporating the ether, 15 g of the product was obtained, dissolved in benzene, and purified further chromatographically by passing on 1500 g of silica gel and eluting with pure benzene. The procedure was repeated with the main fraction. The purified product gave a single spot in thin-layer chromatography (E. Merck, Germany, chromatographic plates). Benzene was removed as far as possible by distilling with a rotational evaporator. The final product was dried under vacuum for 48 hr at  $50^{\circ}\text{C}$  and stored under vacuum over a mixture of calcium chloride/phosphorous pentoxide to give 11 g of the product.

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