The Structure of the α-Methylstyrene Tetramer

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RECENTLY we reported[1] the synthesis of a new type of poly-(α-methylstyrene) by coupling together units of the tetrameric dianion of α-methylstyrene. The structure suggested for this polymer was based on that of the tetrameric dianion, which was formulated by Szwarc *et al.*,[2] as (I) on thermodynamic considerations.

However Szwarc's evidence is not conclusive and we have examined the alkali metal–α-methylstyrene system in some detail. During this work, Berger *et al.*,[3] published results apparently supporting Szwarc's formula but we believe their interpretation to be wrong.

The tetramer was prepared by reaction of α-methylstyrene in tetrahydrofuran with sodium mirrors[4,5] but with a variety of temperatures and contact times. The resulting system was 'killed' by addition of water and the hydrocarbon product was examined by thin-layer chromatography.

Two minor and one major fraction in that order of elution were obtained, together with a small residue on the origin. The separated fractions gave single spots on rechromatographing, but were further purified by molecular distillation *in vacuo*. Mass spectra and high resolution n.m.r. spectra of the fractions were measured. The major fraction, which was a waxy solid, gave a strong parent peak at $m/e = 474$ corresponding to the tetramer, while the minor fractions had equally strong parent peaks at $m/e = 356{\cdot}2505$ ($C_{27}H_{32}$ requires 356·2504) and at $m/e = 238{\cdot}17$ ($C_{18}H_{22}$ requires 238·172) corresponding to the trimer and dimer, respectively. The same dimer was subsequently prepared in better yield by using sodium–potassium alloy instead of a sodium mirror.[5]

The 60 Mc./sec. n.m.r. spectra are shown in the Figure, substantially similar spectra being obtained at 100 Mc./sec. The spectrum of the dimer is consistent with formula (II), showing absorptions at τ 2·92 (Ph), 7·48 (CH), 8·56 (CH_2), and 8·87 (CH_3) in the intensity ratio 5 : 1 : 2 : 3. The trimer spectrum shows similar absorptions but the Ph : CH : (CH_2 + CH_3) ratios are 7·5 : 1 : 6·5 and there is a new absorption of intensity 1 at τ 8·2 which can be assigned to CH_2, β to two phenyl groups. The tetramer spectrum closely resembles that of the trimer but the Ph : CH : (CH_2 + CH_3) ratio is 10 : 1 : 8, with the new absorption at τ 8·2 of intensity 2. The spectra of the trimer and tetramer closely resemble those reported for 2,4,6-triphenylheptane,[6] 2,4-diphenylpentane,[7] and isotactic polystyrene[7] both with respect to fine

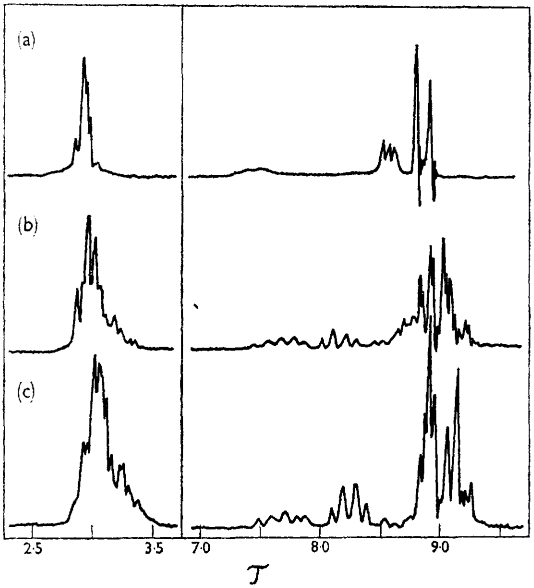


FIGURE. 60 *Mc./sec. n.m.r. spectra of (a) dimer, (b) trimer, and (c) tetramer in* CS_2 *solution, tetramethylsilane as internal indicator.*

structure and chemical shifts, all of which contain CH_2 groups β to two phenyl groups.

The trimer must therefore have formula (III), whilst (IV) or (VI) are the only possible structures for the tetramer on n.m.r. evidence alone, formula (V) being eliminated.

The choice of formula (IV) as the tetramer structure and confirmation of the dimer and trimer structures comes from their mass spectra.

The dimer spectrum shows peaks at 105, 119, and 133 corresponding to the fragments $[Ph{\cdot}CHMe]^+$, $[Ph{\cdot}CHMe{\cdot}CH_2]^+$ and fragment (VII). The trimer shows similar fragmentations with peaks at 105, 119, 133 corresponding to those of the dimer and other peaks at 223, 237, and 251 which are $[p-133]^+$, $[p-119]^+$, and $[p-105]^+$, respectively. There is in addition, a strong peak at 238 resulting from rearrangement of the parent ion and loss of α-methylstyrene.

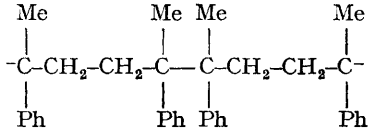
$356^+ \rightarrow 238^+ + 118$ metastable peak at 159·2 (Calc. 159·2). The presence of the 133 peak in the dimer and trimer spectra is significant since it establishes that ion (VII) is a stable one.

The spectrum of the tetramer shows skeletal fragment peaks at 105, 119, 131, 223, 237 but in addition has peaks at 356 and 238 corresponding to the successive loss of two α-methylstyrene molecules by the process:

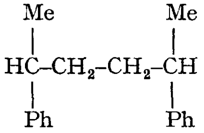
$474^+ \rightarrow 356^+ + 118$ metastable peak at 267·4 (Calc. 267·3),

$356^+ \rightarrow 238^+ + 118$ metastable peak at 159·2 (Calc. 159·2).

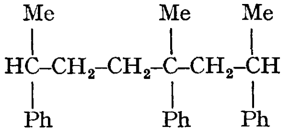
The absence of a peak at 341 corresponding to structure (VIII) suggests that formula (VI) can be eliminated as a structure and this is confirmed by the absence of the peak at 133 corresponding to ion (VII). This latter also eliminates formula (V) as a possible structure.



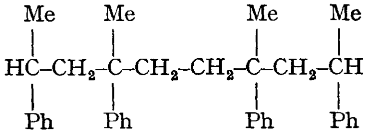
$$-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}- \qquad \text{(I)}$$



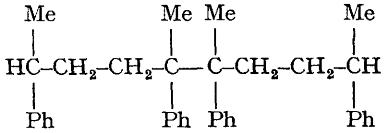
$$\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{H} \qquad \text{(II)}$$



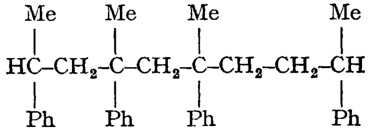
$$\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{H} \qquad \text{(III)}$$



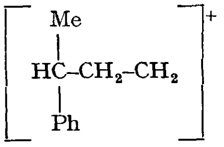
$$\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{H} \qquad \text{(IV)}$$



$$\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{H} \qquad \text{(V)}$$

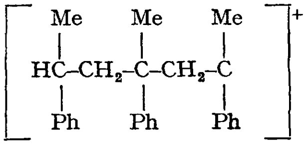


$$\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{H} \qquad \text{(VI)}$$



$$\left[\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}\right]^+$$

(VII)



$$\left[\mathrm{H}\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{C}}}\right]^+$$

(VIII)

We have so far been unable to synthesise the tetramer of structure (V) reported by Szwarc *et al.* The evidence for this was the observation of different equilibrium concentrations of α-methylstyrene in contact with the tetramer anion, but it is possible that these are due to a gegen-ion effect since in one instance this was Na^+ and in the other K^+.

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