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THE REACTION OF *t*-BUTYL CHLORIDE WITH "LIVING" POLY-α-METHYLSTYRYL SODIUM IN TETRAHYDROFURAN

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Abstract—The solid reaction products obtained from the reaction between α-methylstyryl sodium "living" ends in tetrahydrofuran with *t*-butyl chloride, at ambient temperatures, have been separated by TLC and examined by UV, IR and NMR spectroscopy. Apart from the expected elimination and substitution products, a new grouping, absorbing UV radiation at 315 nm, is found in the polymer. IR and UV data suggest that the new grouping is of a quinonoid type structure. Several mechanisms, in explanation of the overall reaction, are discussed in the light of these results.

INTRODUCTION

The reaction of "living" polystyryl and poly-α-methylstyryl sodium and potassium with *t*-butyl chloride in dioxan and tetrahydrofuran (THF), at temperatures between 12° and 40°C, followed a first order rate law.[1,2] Though the kinetics were simple, some complications arose in the reaction product. The reactions of "living" ends with *t*-alkyl halides would be expected to give either elimination, substitution or both reactions in competition. Such a conclusion follows from Ingold[3] and others on the reaction of strong bases with alkyl halides. Analyses of the products of the reaction of "living" poly-α-methylstyryl, polystyryl sodium and potassium in dioxan and THF with *t*-butyl chloride indicate that in addition to elimination and substitution, other reactions occur. Three major pieces of evidence exist for the extra complication: isobutane is formed; the terminated polymer contains some grouping giving rise to a UV absorption at 315–320 nm; there is an increase in molecular weight when the terminating agent is *t*-butyl chloride though not *n*-butyl chloride.

Clarke,[4] in an examination of the reaction forming isobutane, was able to show that when polystyryl sodium and *t*-butyl bromide were reacted in dioxan, in the presence of styrene or α-methylstyrene monomer, the yield of isobutane in the products was reduced. This reaction was accompanied by a reduction in the yield of isobutene by an exactly equal amount. In the cases where styrene monomer was added to the system Ps^-Na^+/t-BuCl/dioxan, (though not α-methylstyrene monomer), new oligomers containing *t*-butyl groups were recovered. It appears therefore, that a reactive intermediate is formed capable of forming isobutane and isobutene in the absence of free monomer and of initiating styrene polymerisation.

In an attempt to identify this reaction intermediate and thus gain an insight into the reaction mechanism, the reaction of the sodium initiated α-methylstyryl "living" ends with *t*-butyl chloride in THF, was chosen for closer study. The reason for this will soon become apparent.

When high concentrations (~ 6–8×10^{-3} M) of "living" poly-α-methylstyryl sodium in THF were reacted with *t*-butyl chloride *in vacuo* to completion at ambient temperatures, the final reaction mixture was not colourless as in the case of the similar reaction in dioxan, but pale orange with a UV absorption at 470 nm. This 470 nm absorbing species thought to be the precursor of the 315 nm species because the absorption disappeared on the exposure to air and was immediately replaced by the new absorption at 315 nm. The "dead" polymer recovered from this system also contained this 315 nm UV absorbing species. The absorption must therefore be associated with a grouping in the terminated polymer. Although the 470 nm UV absorption was absent in the similar system in dioxan, the terminated polymer still contained this new 315 nm absorption. Naphthalide initiated polymer, after termination with *t*-butyl chloride also contained this absorption.

In contrast, "living" polystyryl and poly-α-methylstyryl sodium and potassium terminated with *n*-butyl chloride or water showed no absorption at 315 nm.[4] Furthermore, the polymer as recovered was initially colourless but on standing exposed to air, slowly changed colour to become pale yellow over several days at room temperature. This corresponds with a gradual broadening of the 315 nm peak to ~320 nm together with a long tail absorption to 400 nm.

Various structures absorbing in this region are considered. Shabati and Pines[6] have shown that the 1,4-dimethyl-1,4-diphenylbutadiene of structure 1 absorbs at 315 nm with an molar absorption coefficient (ϵ) of $38 \times 10^3\ lm^{-1}\ cm^{-2}$. Bartlett and Nelson,[5] whilst

PhMeC═CH—CH═CMePh

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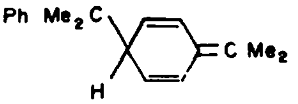
working with azocumene, found two species, structures 2 and 3, which absorbed at 315 nm (quinonoid type structures).



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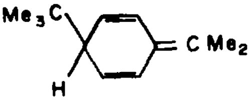

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Structure 2 was formed from cumyl radicals and structure 3 from *t*-butyl radicals in cumene. Since the GLC and NMR analyses of the gaseous and solid products could account for ~95% reaction as occuring by simple elimination and substitution at ambient temperatures, only 2–5% of the "living" ends react in this way and therefore the amount of the 315 nm absorbing species must be small.

The isolation and identification of 315 nm UV absorbing grouping, although present in small amounts, should give an insight into the mechanism operating in these reactions, be it radical, metal halogen exchange or ionic.

EXPERIMENTAL

Sodium initiated poly-α-methylstyryl "living" ends in tetrahydrofuran (6–8 × 10^{-3} M, 120 ml) were prepared in the manner described by other workers[7] and terminated with purified *t*-butyl chloride (2 ml) at room temp. under high vacuum. At the end of the reaction, the THF and excess of *t*-butyl chloride were removed by distillation leaving the solid polymer/salt mixture behind. The polymer mixture was then dissolved in benzene, washed with water in a separating funnel to remove the salt, and finally filtered. The filtrate was placed in a vacuum oven at 50°C for 8–12 h to remove benzene and all traces of unreacted monomer. At this stage, UV and molecular weight measurements, were made on the product.

Separation of oligomers of α-methylstyrene. The mixture of solid polymeric products obtained from the reaction were separated by preparative thin layer chromatography[8,9] (TLC), and each component was subsequently analysed by UV, IR and NMR spectroscopy. In both quantitative and qualitative work polymer solutions in benzene (10%) were made up and applied as a band from a 1 ml spreader.

UV Spectra. The polymer samples were dissolved in chloroform and spectral measurements made on a Unicam SP 500 spectrophotometer.

IR Spectra. A Perkin–Elmer 457 spectrometer calibrated with indene was used to obtain spectra of the polymer samples in thin films.

NMR Spectra. Spectra were measured on a Perkin–Elmer R10 spectrometer at 60 MHz. Solutions in deuterated chloroform were used with tetramethylsilane as internal standard.

RESULTS

The result of the UV measurement on the polymer fraction obtained from the reaction is shown in Fig. 1. The result shows that there are two maxima. These occur at 255 and 315 nm, the absorption at 255 nm being due to that of the phenyl groups and the 315 nm absorption, that of the new grouping in the polymer. The result of the fractionation of the terminated polymer by TLC (double elution) is shown in Fig. 2. The Bands designated 1, 2 and 3 were recovered by scraping them from the plates followed by extraction with diethyl ether and finally filtration to remove the substrate. Molecular weight measurements were made on the extracts dissolved in benzene using the technique of vapour phase osmometry. From ~0.5 to 0.6 g of material added to a single plate, the quantities recovered were: Band 1, 462 mg, Band 2, 36 mg and Band 3, 15 mg. Because the

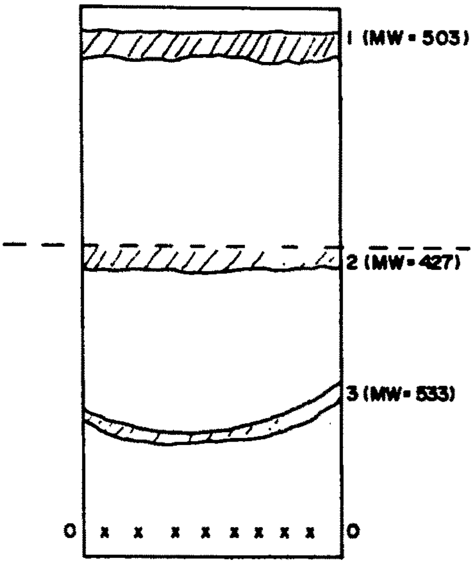


Fig. 2. Chromatogram of terminated polymer. Sample: terminated polymer dissolved in benzene. Solvent: benzene: benzene methanol (5%) Conditions: chromatogram viewed under UV light. Development using unlined tanks. Substrate: silica gel G.

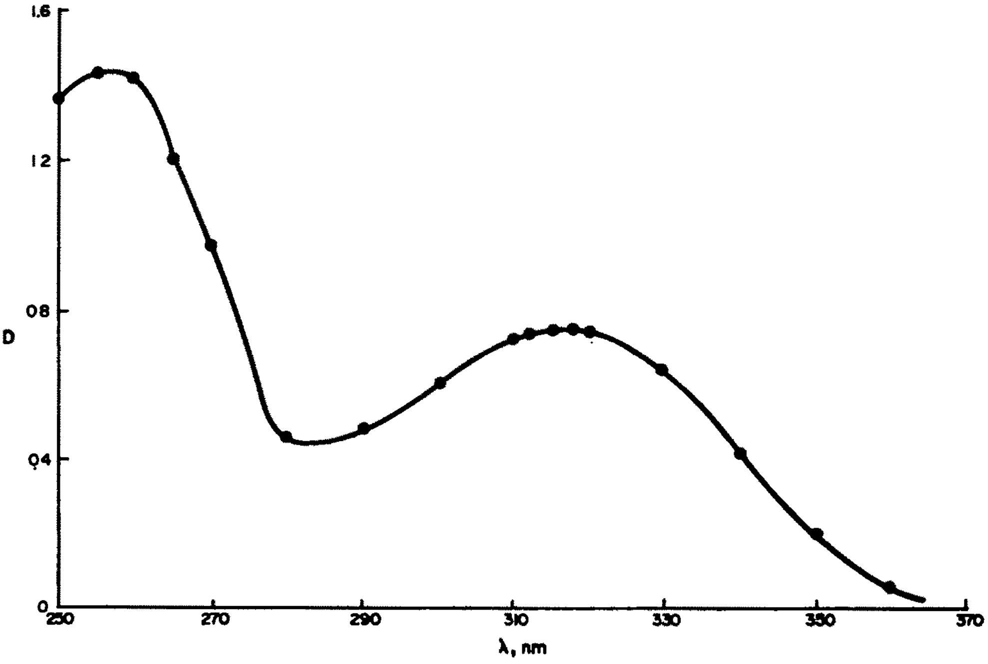


Fig. 1. UV Spectrum of polymer extract.

material recovered from a single plate was insufficient to allow for accurate molecular weight and other measurements, several plates were developed simultaneously and the combined scrapings used in subsequent measurements.

The UV data of the Bands 1, 2 and 3, recovered from the TLC plates, are shown in Fig. 3. The results show that for fractions 1 and 3, only a single λ_{max} is visible over the wave length range studied. Fraction 2, however, has a maximum absorption at 255 nm and a broad absorption at 315 nm, noticeably different from the original absorption maximum.

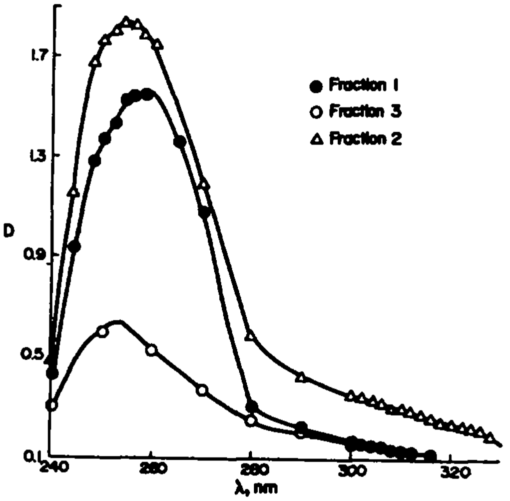


Fig. 3. Spectra of fractions 1, 2 and 3.

Comparing the behaviour of pure H-ended tetramer under the same chromatographic conditions, indicated that Fraction 1 was essentially the same species; the molecular weight of 503 compared to the theoretical value of 474, supported this belief. The bands were further re-chromatographed to check if they were single components. When this was done, Fraction 1 (462 mg) was resolved into one major and two minor components, 1 A(372 mg, major; Mol. Wt. 484), 1 B(45 mg, minor; MW994) and 1 C(22 mg, minor; MW 1153) Fraction 2 separated into three components, 2A, 2B and 2C. Fraction 3 could not be further resolved and is therefore a single component.

The results of the UV analyses of the components separated from fraction 2 are shown in Fig. 4. The spectra show that whilst component 2B and 2C both have maximum absorptions at 255 nm and shoulders at 315 nm, component 2A has only the single maximum absorption at 255 nm. In contrast to 2B and 2C, and like 2A, the components obtained from Fraction 1 have only the single absorption at 255 nm due to the phenyl group. Since both Fractions 2B and 2C contained the 315 nm UV absorbing species, they were selected for further more detailed analyses.

DISCUSSION

Fraction 1. Molecular weight measurements on the components 1A, B and C suggest that component 1A(MW, 484), the major component, is the α-methylstyrene di-hydrogen ended tetramer since its molecular weight compares well with the theoretical value of 474. The IR spectrum of 1A supports the molecular weight data in confirming the tetrameric structure (Fig. 5).

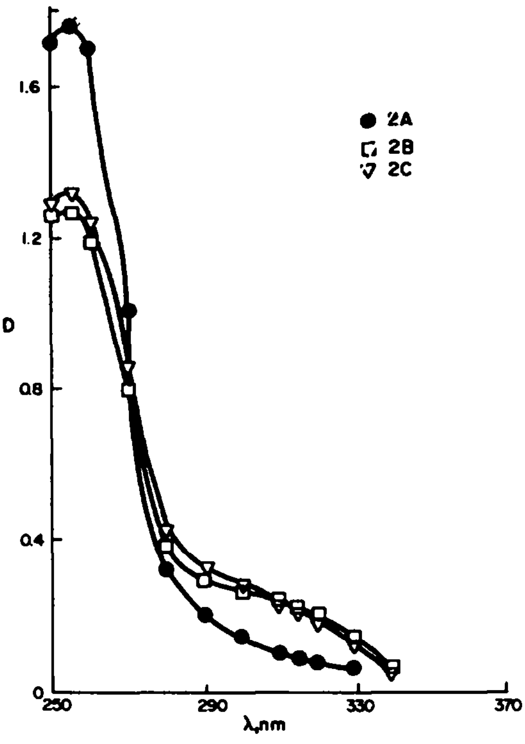


Fig. 4. Spectra of fractions 2A, 2B and 2C.

Further confirmation is obtained from the NMR spectrum of the compound where typical phenyl alkane absorptions occur at $\tau = 2.9$ (due to phenyl groups), 7.7 (from CHα to phenyl groups) and 8.2 (due to CH_2 groups β to phenyl groups).

Fraction 3. The molecular weight value of 533 of this fraction suggests that the compound is the butyl and hydrogen ended tetramer since this value is in good agreement with the theoretical value of 531. The NMR analysis of this compound also suggests that this fraction is correctly assigned. The spectrum has absorptions at 2.84 τ due to phenyl groups, 8.88 τ from CH_3β to the phenyl group and 9.12τ due to the *t*-butyl grouping. The *t*-butyl/H ended structure requires an aromatic: aliphatic ratio of 3:2 which is also the ratio calculated from the spectrum.

Fraction 2. The UV spectra of the components 2A, B and C indicated that the 315 nm absorbing species was contained only in components 2B and 2C. The IR spectrum of one component, 2C, is shown in Fig. 5. A partial list of the IR absorptions is given in Table 1. The table shows that components 2B and 2C are identical and that they are not too dissimilar from the typical di-hydrogen ended tetramer. However, the spectra differed from that for typical phenyl alkanes with normal alkyl and mono-substituted phenyl frequencies in that extra absorptions were observed at the frequencies 1720, 738, 841 and 2250 cm^{-1}. While the 1720 cm^{-1} absorption seems likely to be due to the presence of carbonyl groups, the other bands can only be assigned tentatively. The 738 cm^{-1} band could indicate C=C unsaturation; in confirmation of this, there is a poorly resolved peak at 1620 cm^{-1}. The peak at 841 cm^{-1} could be assigned to a *para*-substituted phenyl group. The 2250 cm^{-1} band could be taken as evidence for C=C though hydrocarbons of structure $Me_3C{-}CHMe{-}CMe_3$ and $Me_2CH{-}CH(C_2H_5)CHMe_2$ show absorption

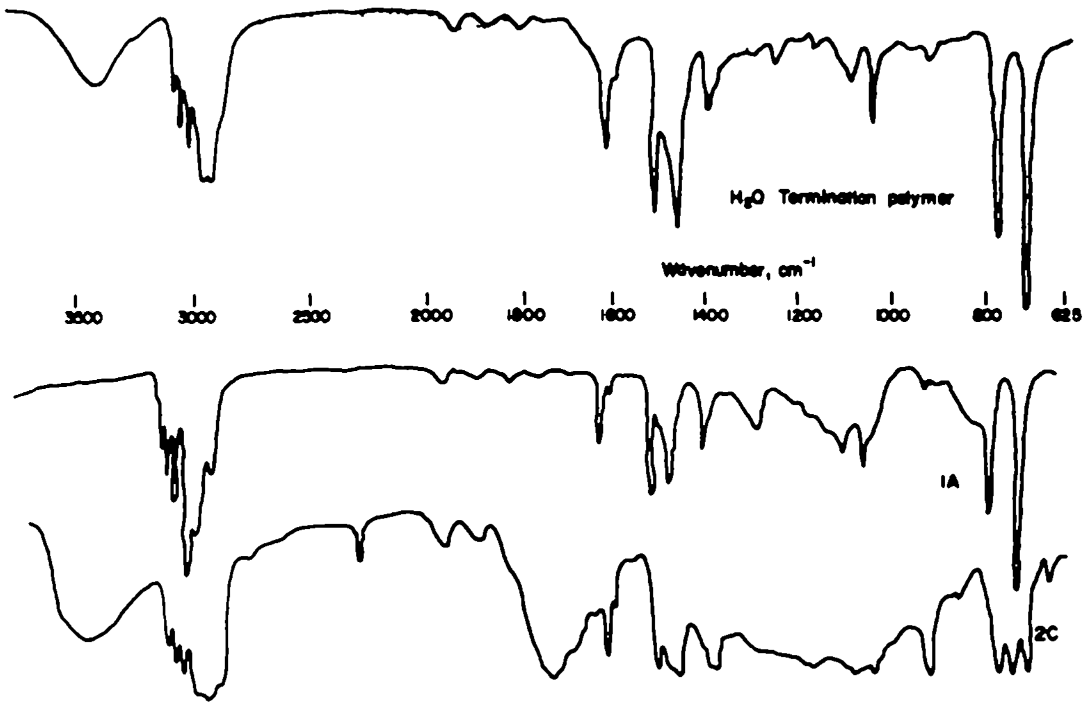


Fig. 5. IR Spectra of terminated polymer.

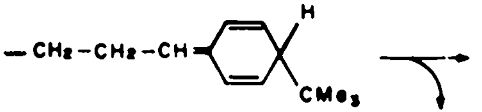
Table 1. Partial IR spectra of components 2B and 2C. Sample (Thin film)

	Tetramer (cm^{-1})	2B (cm^{-1})	2C (cm^{-1})
γCH aromatic	3103w	3103w	3103w
	3085m	3085m	3085m
	3060ms	3060ms	3060m
	3027s	3027s	3027s
	3000w	—	—
γCH_3	2960vs	2960s	2960s
γCH_2	2926vs	2930s	2930s
γCH_3	2869m	2870m	2870m
γ_{ring}	1603ms	1600s	1600m
	1494vs	1492s	1492m
$\delta CH_3/CH_2$	1452vs	1452ms	1452ms
δCH_3	1379ms	1380ms	1380m
δ aromatic	761vs	760m	760m
	699vvs	701s	701m
Other groups		730m	650w
		841w	841w
		1720s	1720s
		2250w	2250ms
		3300–3700	3300–3700

here.[10] A doublet vibration occurs at 1380 cm^{-1} and together with a weak skeletal vibration at 1170 cm^{-1} is identified as a dimethyl group of possible structure Me_2CH-. The typical broad absorptions at 3300–3700 cm^{-1} are identified as the hydroxy (OH) absorptions. No OH absorptions were observed in the tetramer 1A.

Some conclusions can therefore be drawn: firstly, it would appear from these results that components 2B and 2C are similar, differing only in molecular weights, and separation on the TLC plate is therefore effected by molecular weight differences only. This in effect means that the new grouping forms a part of polymer chains of varying lengths. Secondly, the new grouping is inherently unstable. The instability of the grouping is supported by the fact that, on standing at room temperature in light, the peak absorption at 315 nm gradually broadened. This broadening of the maximum absorption coincided with the yellowing of the polymer.

These results might be explained by postulation that the quinonoid structure 4 absorbing at 315 nm may form initially, (the immediate disappearance of the 470 nm absorption on exposure to air to give the 315 nm species supports such an idea where a quinonoid type ion is expected to absorb at 470) and, not being stable, breakdown to give structure 5



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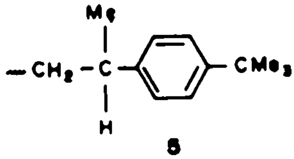

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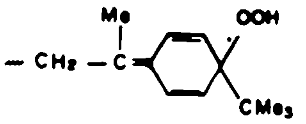
or oxidise to give structure 6 which may breakdown further:



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The oxidation product 6 and further oxidised products could explain the carbonyl and hydroxy absorptions noted in the IR spectrum.

Mechanistic implications. If the reactions are predominantly ionic, then in view of the known reactions of strong bases with *t*-alkyl halides, the reactions must be essentially two competing reactions leading to elimination and substitution thus:

$$\mathrm{P\alpha^-Na^+} + t\text{-BuCl} \xrightarrow{k_s} \mathrm{P\alpha} - t\text{-Bu} + \mathrm{Na^+Cl^-}$$

$$\mathrm{P\alpha^-Na^+} + t\text{-BuCl} \xrightarrow{k_e} \mathrm{P\alpha - H + CH_2{=}CMe_2 + Na^+Cl^-}$$

To these two reactions a third step must be added to account for the production of *iso*butane. This third step could be accounted for by postulating a metal halogen type mechanism thus:

$$\mathrm{P\alpha^-Na^+} + t\text{-BuCl} \longrightarrow \mathrm{P\alpha - Cl} + t\text{-Bu}^-\mathrm{Na^+}$$

$$t\text{-Bu}^-\mathrm{Na^+} + t\text{-BuCl} \longrightarrow \textit{Iso}\text{butane} + \mathrm{Na^+Cl^-} + \textit{Iso}\text{butane}$$

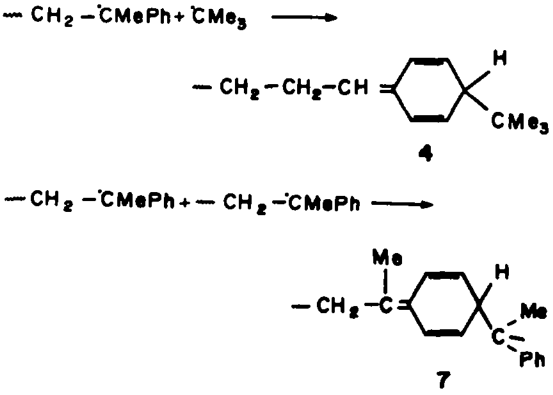
If a reaction between living ends and *t*-butyl chloride occurs by electron transfer, then the outcome of such a process would be two radicals thus:

$$\mathrm{P\alpha^-Na^+} + t\text{-BuCl} \longrightarrow \mathrm{P\alpha^{\cdot}} + t\text{-Bu}^{\cdot} + \mathrm{Na^+Cl^-}$$

Further reaction of the radicals would be expected to give rise to isobutane and *iso*butane and *iso*butene. Alternatively, the reaction could occur through a hydride ion intermediate such as sodium hydride ($\mathrm{Na^+H^-}$). The reaction of $\mathrm{Na^+H^-}$ with *t*-BuCl could explain the formation of isobutane. However, the hydride mechanism seems unlikely because aged "living" end solutions in which the hydride ion is known to form,[11,12] did not produce, when reacted with *t*-butyl chloride, correspondingly more isobutane, nor did reactions with *n*-alkyl halides produce significant yields of *n*-alkanes.[4]

While the formation of a 1,4-dimetyl-1,4-diphenyl butadiene of structure 1, when poly-α-methylstyryl potassium dimer reacts with *t*-butyl chloride, is not difficult to postulate, it is more difficult to envisage a similar reaction with tetramer or indeed long chain polystyrene.

Both the ionic and electron transfer mechanisms could be used to explain the formation of quinonoid type structures. If some of the reaction occurs through a radical mechanism, then the following reactions could occur:



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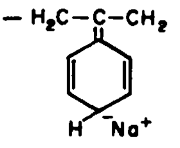
By analogy with the studies on cumyl radical combination,[6] such reaction would only occur to a slight extent.

The formation of the quinonoid type structure may be postulated to occur ionically if it is assumed that the reaction occurs partially through the quinonoid anion 8



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giving structure 4 by a substitution reaction on *t*-butyl chloride.

The TLC analysis is a consistent with the GLC data obtained by Clarke[4] since the major component recovered from the plate was the dihydrogen ended tetramer which could only form through elimination. Since components 1B and 1C were of molecular weights roughly two and three times the molecular weight of the tetramer, the result suggests that some coupling of the polymer molecules did occur during the reaction. This coupling of the polymer to form higher molecular weight species lends supports to the electron transfer mechanism since in a radical process, polymer radicals would be expected to react in this way. This mechanism is further supported by the fact that new styrene oligomers were recovered when styrene monomer was used to scavenge the reaction intermediate. However, there are two factors militating against such a mechanism; (a) no ESR signal could be detected and (b) likewise, no GLC peak for di-*t*-butyl, expected from the combination of two *t*-butyl radicals, could be detected. It could be that all the reactions take place inside a cage of solvent molecules which prevents radicals from diffusing out of the cage, or, that the radicals are present in very low concentration or even a combination of both these factors.

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REFERENCES

[1] A. R. Baker and G. C. East, *Polymer* 14, 649 (1973).
[2] H. A. Ellis, Ph.D. Thesis, University of Leeds (1976).
[3] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd Edn. Bell, London (1969).
[4] J. W. Clarke, Ph.D. Thesis, University of Leeds (1976).
[5] J. Shabtai and H. Pines, *J. Org. Chem.* 26, 4225 (1961).
[6] S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.* 88, 137 (1966).
[7] C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.* 66, 904 (1962).
[8] E. Stahl, *Thin Layer Chromatography*. Academic Press, London (1965).
[9] E. V. Truter, *Thin Film Chromatography*. Leaver-Hume Press, London (1963).
[10] (Edited by H. A. Syzmanski). *Infra Red Handbook*, Plenium Press, New York (1963).
[11] M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Processes*. Interscience, New York (1968).
[12] B. J. Schmitt, *Makromol. Chem.* 156, 243 (1972).