Table II
Theta Temperatures of Some Modified Polystyrenes in Cyclohexane

Polymer	Mol % added groups	Location	θ, °C	$\overline{M}_w \times 10^{-5}$
SBS-1	1.77	Center	31.8	1.51
SIS-1	1.57	Center	32.0	0.31
$C4bbCH_2Cl$	1.47	Random	38.2	1.38[b]
$C3bbCH_2Cl$	3.88	Random	44.0	1.57
$C5bbCH_2Ac$	1.77	Random	43.2	1.53
$C3bbCH_2Ac$	3.88	Random	49.3	1.58
CObb3c[a]	1.93	Random	41.0	1.58

[a] A fraction of a random styrene–vinyl acetate copolymer described in ref 12. [b] $\overline{M}_w$ of the original polystyrene (unmodified) was 134 000.

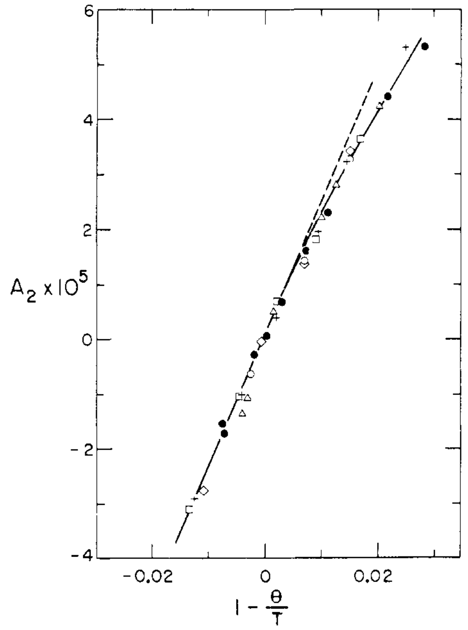

Figure 3. Second virial coefficient in cyclohexane as a function of temperature: (●) C_4bb; (◇) C_4bbCH_2Cl; (○) C_3bbCH_2Cl; (□) C_3bbCH_2Ac; (+) C_5bbCH_2Ac; (△) SBS-1.

normal groups, that the heat of dilution is roughly twice as great for chloromethylated groups and about half as great for diene groups as for normal polystyrene units.

Depression of the theta temperature ($A_2 = 0$) has been noted for comb[13,14] and star polystyrenes.[11,15] This effect has been attributed to the high segment density in such polymers.[16] The present work indicates the possibility of another effect connected with changes in $\Delta \overline{H}_1$ at the junction points. The latter points have the properties of a foreign group whose nature depends on the coupling reaction used. This effect could be important particularly at low molecular weights. The presence of unreacted chloromethyl groups in incompletely coupled comb polystyrenes would affect θ but in the opposite direction to that normally observed in comb polymers. In one case[11] up to 1% of isoprene units were present at the junction point of some star polystyrenes to facilitate the coupling reaction. The θ depression was observed however in the absence of isoprene and in addition the maximum effect on θ would be 2° in the polymer of lowest molecular weight where the percentage of isoprene reached 1%.

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Radiation-Induced Pyrolysis of Poly(α-methylstyrene). Formation of 1,1,3-Trimethyl-3-phenylindane by an Ionic Chain Reaction

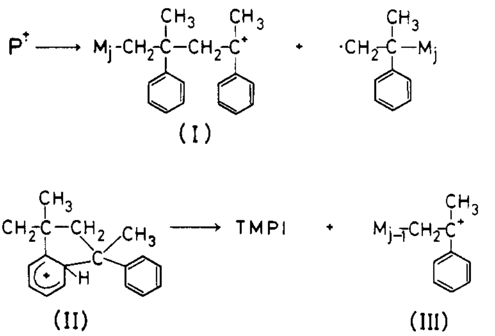
We wish to report an ionic chain reaction which occurs during the radiation-induced pyrolysis of poly(α-methylstyrene) and results in the formation of a dimer, 1,1,3-trimethyl-3-phenylindane (TMPI). Pyrolysis of poly(α-methylstyrene) under vacuum, where the decomposition by a radical chain reaction is important, was studied long ago, and it is known that below about 400 °C polymer decomposes almost completely into monomer.[1] The present investigation on the radiation-induced pyrolysis is concerned with the decomposition by ionic reactions initiated by irradiation at high temperature. Poly(α-methylstyrene) powder was evacuated at a pressure of 10^{-6} mm for 24 h in a Pyrex tube equipped with a cold finger and then sealed.[2] The sample was heated at 200 °C under irradiation of ^{60}Co γ rays (the dose rate, 9.2×10^5 rad/h), and the volatile products were collected in the cold finger which was cooled with liquid nitrogen and protected by a leadblock from radiation. The products both trapped in the cold finger and remaining in the irradiated polymer were analyzed with a gas chromatograph using a Apiezon L column.

It was found that the products almost exclusively consist of monomer and a dimer, TMPI, while the only product detected was monomer when heated at 200 °C in the absence of radiation. The dimer was identified by its nmr spectrum [$\tau(CCl_4)$ 2.91 (9 H, m), 7.56 (1 H, d, J = 13 Hz), 7.89 (1 H, d, J = 13 Hz), 8.39 (3 H, s), 8.71 (3 H, s), 9.00 (3 H, s)] and mass spectrum (M^+ at m/e 236). The dimer produced was also contained in the irradiated polymer and the amount of the dimer remaining in the polymer was comparable with that trapped in the cold finger, while the monomer almost completely passed over into the cold finger. The total yield of the dimer was proportional to the irradiation time in the range studied, up to 3 h. The G value of the dimer was 34, and such a high yield suggests that it is formed by a chain reaction. When the polymer was irradiated at room temperature or heated at 200 °C after irradiating at room temperature, the yield of TMPI was much smaller, G(TMPI) < 1. Thus, it is indicated that the chain reaction generating TMPI occurs at high temperature under irradiation.

TMPI is known to be formed in the acid-catalyzed dimerization of α-methylstyrene together with linear dimers.[3] It has also been reported that in the cationic polymerization of α-methylstyrene by catalyst a 1,3-dimethyl-3-phenylindanyl end group is formed by the electrophilic substitution of the penultimate benzene ring by the propagating cation.[4] These facts suggest that the dimer is formed by the reaction of the carbonium ion produced by irradiation.

Usually, in the radiolysis of hydrocarbons the effect of the addition of a cation scavenger such as ammonia, alcohol, or ether on product yields is examined in order to obtain evidence for the cationic processes of product formations. In the present investigation poly(isobutyl vinyl ether) was used as a cation scavenger because any volatile additive is not suitable for the reaction at high temperature under vacuum. The yield of the dimer was reduced to less than one-third by the addition of about 3 wt % of poly(isobutyl vinyl ether).[5] The incomplete inhibition of the dimer formation is probably due to the low mobility of the reaction sites in the solid polymer. Thus, it can be concluded that the dimer is formed via a cationic process. The proposed mechanism is as follows:

$$P \rightsquigarrow P^{+} + e$$



where P and M denote a polymer chain and a monomer unit, respectively. The stable tertiary carbonium ion (I) is produced from the polymer cation, $P\cdot^{+}$, and the chain end cyclizes by the carbonium ion substituting the penultimate phenyl ring to give II analogously to the propagating chain end in the cationic polymerization.[4] The carbonium ion III produced by the last step again yields the dimer similarly to I.

The last step of the scheme, which is regarded as an intramolecular protolysis of the C– bond by the proton derived from the aromatic ring, should require a high activation energy. The protolysis of a C–C bond has recently been reported in the study using superacid.[6] The result of the present study seems to suggest that at high temperature the protolysis of the weak C–C bond generating the stable tertiary carbonium ion occurs by such a weak acid as the benzenium ion.[7]

Cationic chain reactions occurring in the radiation-induced pyrolysis have been reported in the ether formations from alcohols[8] and the decomposition of n-butane.[9] The dimer formation from poly(α-methylstyrene) should be one of the examples of such ionic chain reactions occurring at high temperature.

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(7) In the radiation-induced pyrolysis of polystyrene under the same condition as that in the case of poly(α-methylstyrene), 1-methyl-1-phenylindane was not produced in a detectable amount, indicating that the chain reaction is not initiated when the intermediate cation is the less stable secondary carbonium ion.

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Phosphorescence Quenching in the Photoreaction of Benzophenone with the *n*-Alkanes. A Model for the Interaction of Small Molecules with Polymers

When a small molecule reacts with a polymer, the kinetics of that reaction can reveal details of the interaction between the two species. In enzyme kinetics, the apparent binding constant of a substrate to the active site can be inferred from a proper treatment of the rate data.[1] In the reaction of ·OH radicals with various polymers, the *chain length dependence* of the second order rate constant has been related to the chain length dependence of the end-to-end distance of the polymer.[2] When the small molecule is sufficiently reactive that it reacts with the polymer on virtually every collision, the corresponding second order rate constant is sensitive primarily to the shape of the polymer.[2] If the small molecule is sufficiently unreactive that it reacts only once every 1000 or more collisions, other facets of the polymer–small molecule interaction are probed.

In this paper we present results of a kinetic study of the reaction between photoexcited benzophenone and a series of n-alkanes, examined in dilute carbon tetrachloride solution. Values of the second order rate constants $k_{\mathrm{obsd}}(n)$ are reported as a function of the alkane chain length. These values provide a unique insight into the nature of encounter complexes involving randomly coiled alkane polymers.

The power of this reaction to provide a glimpse at details of a polymer–small molecule interaction derives from three facets of hydrogen abstraction reactions: (a) each of the CH_2 groups in the alkanes are equally reactive toward benzophenone triplets;[3] (b) the methyl groups are relatively unreactive; and (c) rate constants for reaction of benzophenone triplets with alkanes are four orders of magnitude slower than the diffusion limit. These factors permit the excited benzophenone (i) to undergo collisions with thousands of alkane molecules before reacting and (ii) to encounter many CH_2 groups in an alkane within one collision complex. The latter factor leads to the prediction that the second order rate constant should increase with increasing chain length of the alkane "polymer".

Benzophenone triplets react with alkanes by hydrogen abstraction to yield a pair of radicals. This reaction is closely related to hydrogen abstraction reactions of *tert*-butyl-O·, Cl·,