CROSSLINKING OF STYRENE HOMOPOLYMERS AND COPOLYMERS BY p-DI(CHLOROMETHYL)BENZENE.

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by

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ABSTRACT.

This thesis is principally concerned with the kinetics of the crosslinking of polystyrene using p-di(chloromethyl)benzene (D.C.M.B.), in the presence of a Friedel-Crafts catalyst, and the effect of this crosslinking on the thermal properties of polystyrene.

As the polymerisation of styrene and the condensation of D.C.M.B. with aromatic nuclei can both be initiated by Friedel-Crafts catalysts, an attempt was made to produce crosslinked polystyrene by mixing styrene, D.C.M.B. and stannic chloride in 1,2-dichloroethane (D.C.E.) at 30°C under vacuum. It was impossible, however, to define a set of conditions under which the two reactions proceed at comparable rates to give the desired product, since the cationic polymerisation of styrene was found to be approximately 150 times faster than the condensation between styrene nuclei and D.C.M.B.

It became necessary, therefore, to condense preformed, low molecular weight polystyrene with D.C.M.B. using stannic chloride as the catalyst in D.C.E. at 30°C under vacuum. The overall degree of crosslinking was followed by HCl evolution and the degree of intermolecular crosslinking was determined by molecular weight measurements. The degree of intramolecular crosslinking was calculated by difference. By plotting the concentration of crosslinks against reaction time, the rate of crosslink formation was obtained for each series of reactant concentrations and by relating the rate of crosslinking to the initial reactant concentrations, the orders of the overall, intermolecular and intramolecular crosslinking reactions with respect to each reactant concentration were determined. The corresponding

rate constants for the overall, intermolecular and intramolecular reactions were also evaluated.

The initial stages of the Friedel-Crafts condensation between toluene and D.C.M.B. in D.C.E. in the presence of stannic chloride, which may be regarded as a model for the condensation of polystyrene with D.C.M.B., was also investigated at 30°C under vacuum. HCl evolution was employed to follow the progress of the reaction, the rate constant and order of the condensation with respect to the initial concentration of each reactant being determined by the methods used for the condensation between polystyrene and D.C.M.B. The rate of crosslinking polystyrene was compared with the rate of formation of p-dixylylbenzene from two toluene molecules and one D.C.M.B. molecule, to yield information concerning the steric effect of polymer molecules on the rate of Friedel-Crafts alkylations.

Information about the effect of crosslinking on the thermal properties of polystyrene was obtained using Differential Thermal Analysis (D.T.A.), Differential Scanning Calorimetry (D.S.C.), Thermogravimetric Analysis (T.G.A.) and Thermal Volatilisation Analysis (T.V.A.). Although D.T.A. and D.S.C. showed that the glass transition temperature increases linearly with the degree of crosslinking, up to the onset of gelation, T.G.A. and T.V.A. indicated that due to increasing strain as the degree of crosslinking increases, the temperature at which thermal degradation commences, decreases.

A preliminary investigation into the condensation of styrene/methyl methacrylate copolymers with D.C.M.B. using stannic chloride as the catalyst in D.C.E. at 60°C under nitrogen, showed that in addition to the Friedel-Crafts alkylation which produces crosslinks as in the case of polystyrene, a Friedel-Crafts acylation occurs between methacrylate ester groups and the ortho position of the adjacent styrene nuclei, producing cyclic ketonic structures. The rate of acylation is affected in the predicted manner by the presence of activating and deactivating substituents in the styrene nuclei. An intermolecular acylation was also shown to occur between homopolymers of styrene and methyl methacrylate. The increase in the thermal stability of the acylated copolymers, with respect to the copolymers, was demonstrated using T.V.A. and this was shown to be a result of the stabilising effect of the cyclic structures in the acylated copolymer chain.

CHAPTER ONE.

GENERAL INTRODUCTION.

1.1 Introduction.

The possibility of preparing polymers by Friedel-Crafts reactions was mentioned as early as 1885,[1] when polymeric materials were reported to be formed by the action of aluminium trichloride on benzyl chloride. Polybenzyl has since been the subject of numerous investigations[2-9] concerning the influence of Friedel-Crafts catalysts on the structure and properties of the polymers. Unfortunately, the polybenzyl polymers are mechanically weak and have little practical value.

More promising results were obtained between 1959 and 1965.[10-13] Aromatic compounds were chloromethylated to give di and tri substituted products which were then either subjected to self-condensation or used as coupling agents for other aromatic compounds, to give polymers. These polycondensations were carried out in the presence of Lewis acids and the materials formed have been termed Friedel-Crafts Polymers.[10] They have many potential applications since they possess considerably greater thermal stability and mechanical strength than the phenolic resins, although they have similar structures consisting of alternating methylene and aromatic units.

Friedel-Crafts Polymers are now commercially available[14] and a large volume of information has been acquired recently about the kinetics of formation and the structure of these polymeric resins.[15-25]

These Friedel-Crafts reactions should be applicable, in principle, as a method of crosslinking linear polymers incorporating aromatic nuclei. Polystyrene is the most obvious example and a new method of producing crosslinked polystyrene may be of considerable advantage industrially as it is widely used in the micro-electronics field, due to its low electric loss characteristics. Some information relevant to this crosslinking reaction will be discussed in the following sections of this chapter.

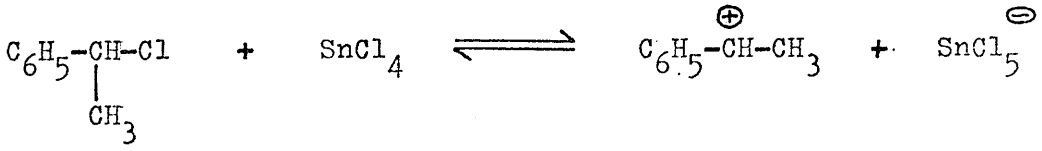
1.2 Cationic Polymerisation of Styrene.

Due to the complexity of cationic polymerisation generally, this section is restricted to a description of the cationic polymerisation of styrene using stannic chloride as catalyst in 1,2-dichloroethane solution. This system is extremely complicated and many inconsistencies still remain to be explained, but in general, the rate of polymerisation is rapid compared with radical polymerisations giving low degrees of polymerisation at ordinary temperatures and higher molecular weights at lower temperatures. The activation energies are very small and the presence of cocatalysts such as water or solvent can have a considerable influence on the rate of the reaction. Qualitative investigations into the cationic polymerisation of styrene were initiated by Staudinger[26] but the first quantitative kinetic study was reported by Williams.[27-29]

Until 1964 it was generally accepted that the cationic polymerisation of styrene involves chain carriers which are carbonium ions derived initially from styrene but there was little direct evidence for the presence of carbonium ions during polymerisation. The theory became firmly established since it accounted satisfactorily for most experimental observations. In interpreting experimental observations, however, it is necessary to distinguish between a demonstration that an olefin can form a carbonium ion in the presence of a catalyst and a demonstration that these ions are the active species in the polymerisation process.

Relatively few attempts have been made to demonstrate the presence of ions during the polymerisation of styrene and Pepper[30] concluded that his conductivity studies on the styrene/stannic chloride system failed to demonstrate the presence of chain propagating cations or their concentration. Dielectric measurements of the same system made by Metz[31] indicated that a steady state concentration of ions was present during the polymerisation but since no rate measurements were made concurrently, his results do not show whether the ions are involved in the polymerisation. Ionic character has, however, been inferred from experimental observations that polar solvents favour the reactions, that Friedel-Crafts catalysts are efficient initiators and more recently Evans[32] has shown that the dimerisation of 1,1-diphenylethylene has an absorption spectrum due to the presence of carbonium ions.

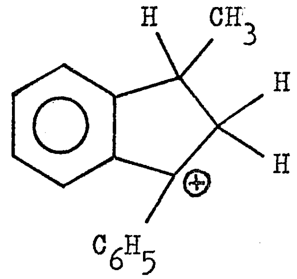
Jordan and Treloar[33,34] compared the spectra of 1-phenylethyl chloride in stannic chloride and of styrene in stannic chloride, in polar media and concluded that the equilibrium involved is,



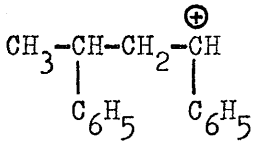
$$C_6H_5\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}Cl \quad + \quad SnCl_4 \quad \rightleftharpoons \quad C_6H_5\text{-}\overset{\oplus}{CH}\text{-}CH_3 \quad + \quad \overset{\ominus}{SnCl_5}$$

the peaks at 410mμ and 300mμ in the ultra-violet spectrum being due to growing polymer ions since no reaction occurred in non-polar media.

Thus these absorptions were thought to be due to the phenylethyl ion, but Bertoli and Plesch[35] showed that the principal originator of the absorption at 425mμ is the 3(1-methyl, 3-phenylindanyl) cation,



The spectrum of the 1-phenylethyl ion has not yet been identified but that of the homologous 1,3-diphenyl-n-butyl cation,



$$CH_3-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{\overset{\oplus}{C}H}}$$

was shown to have only one important absorption at 315mμ.[35] Thus, although the original theory of the polystyryl cation as the chain carrier has been questioned, a mixture of chain carrying cations must be possible.

Pepper[36-42] has shown that the cationic polymerisation of styrene, catalysed by perchloric acid in polar solvents, follows simple kinetics which can be interpreted in terms of fast initiation and slow propagation,

$$\begin{array}{lll} P_1 + C \longrightarrow M_1^{\oplus}\,C^{\ominus} & & \text{initiation} \\ M_n^{\oplus}\,C^{\ominus} + P_1 \longrightarrow M_{n+1}^{\oplus}\,C^{\ominus} & & \text{propagation} \\ M_n^{\oplus}\,C^{\ominus} \longrightarrow P_n + C & & \text{termination or transfer} \end{array}$$

where C is the catalyst, or catalyst/cocatalyst complex which is described in Chapter 3. Gandini and Plesch[43-46] compared spectral and conductivity measurements with rate measurements for the above system. Unexpectedly, their results suggested that the chain carriers are not ionic. As they are highly polar and in many respects behave as if they are ionic, the polymerisations were termed pseudo-cationic. Plesch proposed that the chain propagating species is an ester formed between the olefin and perchloric acid and is stabilised by complexing with four styrene molecules.

Before the discovery of pseudo-cationic reactions in 1964, it could be said that the function of the cocatalyst was to provide cations to initiate polymerisations[47] and although this is still valid for true cationic polymerisations, Plesch suggests that the cocatalyst is essential in the formation of the ester and thus has a similar function.

The discovery of pseudo-cationic polymerisations, therefore, necessitates a reassessment of the results in this field but as no further investigations have been carried out on the styrene/stannic chloride/1,2-dichloroethane system, it must be assumed that the carbonium ion theory is still applicable, until disproved.

Although the rate of polymerisation in polar media is greater than in non-polar media, this is not simply related to the dielectric constant of the medium. Other factors including the polarisability of solvent molecules and their solvating power for ion-pairs are also very important.

The polymerisation in 1,2-dichloroethane was first studied by Pepper[48] who found the following rate relationship,

$$\text{Initial Rate} \propto (\text{Styrene})^{2.3}(\text{SnCl}_4)$$

Okamura and Higashimura[49] later observed the initial and internal rate equations to be different, the change-over occurring at about 30% conversion.

$$\text{Initial Rate} \propto (\text{Styrene})^{2.4}(\text{SnCl}_4)$$
$$\text{Internal Rate} \propto (\text{Styrene})^{2.0}$$

It was impossible to obtain the dependence upon stannic chloride concentration for the internal rate equation. Further investigations by Colclough and Dainton[50,51] in the presence of t-butyl chloride, which is a cocatalyst, showed that,

$$\text{Initial Rate} \propto (\text{Styrene})^{2.0}(\text{SnCl}_4)(\text{t-BuCl})$$

and confirmed Pepper's mechanism with modifications for the presence of a cocatalyst.

Thus, although the main features of the kinetics and mechanism of the stannic chloride catalysed polymerisation of styrene in 1,2-dichloroethane are well established[52] further investigations are required to explain the inconsistencies.

1.3 Thermal Degradation of Polystyrene.

Pyrolysis of polystyrene between 300 and 400°C under vacuum yields approximately 42% monomer, together with progressively decreasing amounts of dimer, trimer, tetramer and pentamer,[53] which are formed by intramolecular transfer at the α-hydrogen atom.[54] During degradation a rapid decrease in molecular weight occurs initially, settling down to a lower rate of decrease after approximately 30%

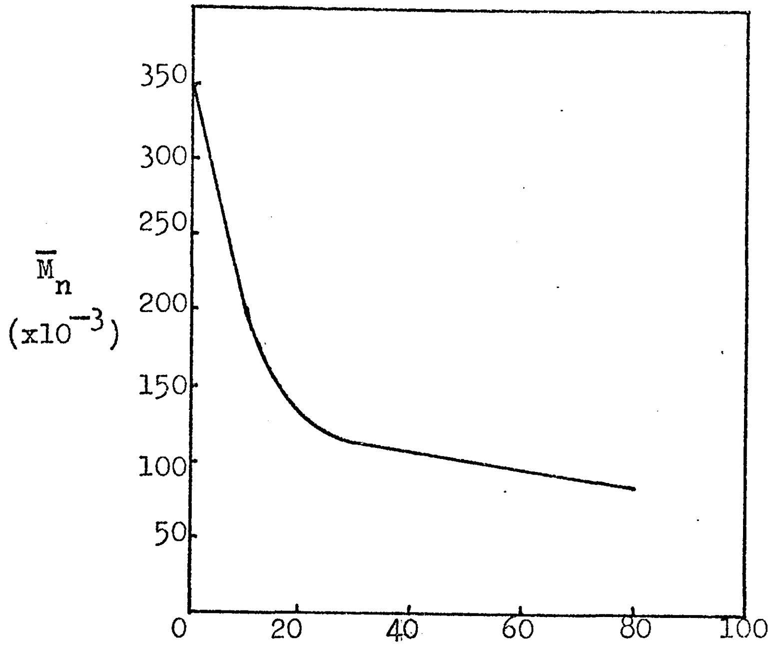


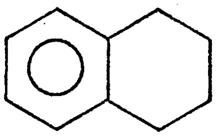
Figure 1. Isothermal Degradation of Polystyrene at 290°C.

volatilisation as shown in Figure 1.[55,56]

There is general agreement about the principal features of the mechanism of the thermal degradation of polystyrene. However, controversy still exists about the reason for the rapid decrease in molecular weight which occurs in the early stages of the reaction. It may be due to intermolecular transfer or to 'weak links' in the polymer structure, although the possible structure of the latter is still in dispute.

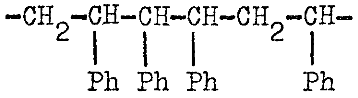
The thermal degradation of polystyrene under high vacuum was first studied by Jellinek,[57] who explained the rapid initial decrease in molecular weight as due to radical scission at a number of 'weak links' randomly distributed along the polymer chain. Alternatively, Madorsky[58] proposed that there is no essential difference between the initial and later stages of the degradation and that the initial fall in molecular weight is predominantly due to intermolecular transfer following chain end initiation. However, from experimental data similar to that of Jellinek, Grassie and Kerr[55,56] deduced that in the initial stages of the reaction, chain scission occurs by the breaking of labile bonds but that active radicals, as suggested by Jellinek, are not produced. Instead, they proposed that stable chain ends are formed at which depolymerisation, as in poly(methyl methacrylate)[59], is not readily initiated until after about 30% volatilisation. In addition, Grassie and Kerr showed by correlation of the method of preparation with 'weak link' concentration, calculated from the extent of the initial decrease in molecular weight, that 'weak links' do not arise from impurities but that they are formed during the preparation of the polymer in a reaction which is in direct competition with the propagation step.

Grassie and Cameron[60-62] have obtained the most convincing evidence for the existence of 'weak links'. They compared the degradation reaction of polystyrene in bulk with the reactions in naphthalene and tetralin solutions. The rates of initial decrease in molecular weight were found to be identical in all three media, but the subsequent decrease in molecular weight is less in naphthalene than in bulk and completely inhibited in tetralin. From this evidence, it was inferred that the radical chain depolymerisation is retarded in naphthalene and inhibited in tetralin due to the radical chain inhibition properties of the α-methylene group in tetralin,



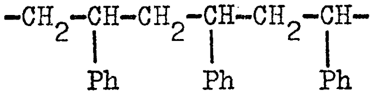
but that 'weak link' scission is unaffected. As this separability of chain scission and depropagation to give volatile products cannot be explained in terms of the intermolecular transfer theory, which implies that there is no essential difference between the initial and later stages of the degradation, this must be taken as strong evidence for the 'weak link' theory.

Although a study of the degradation of styrene/stilbene copolymers eliminated the possibility of head to head linkages,



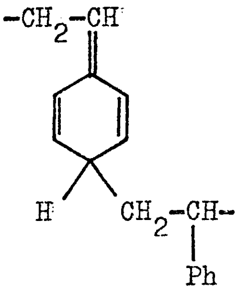
$$-CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-\underset{\displaystyle Ph}{\underset{|}{CH}}-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-$$

Grassie and Cameron were unable to identify the correct nature of the labile structures. They suggested, however, that in addition to the normal head to tail linkages in polystyrene,



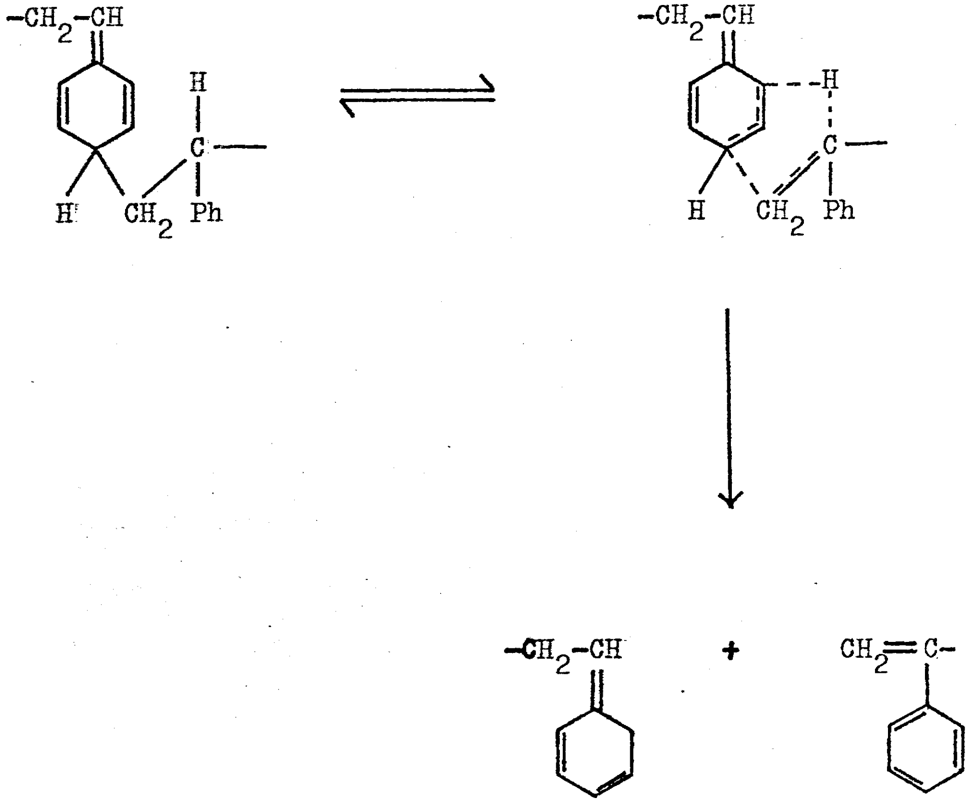
$$-CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Ph}{\underset{|}{CH}}-$$

addition of monomer during propagation could result in structures of the type,



which are similar to the ketenimine structures known to constitute 'weak links' in poly(methacrylonitrile).[63]

Chemical and spectroscopic evidence for this type of structure have not been obtained due to the low concentrations involved, but a radiochemical investigation[64] has demonstrated that radically initiated polystyrenes do incorporate main chain unsaturation, and further evidence for unsaturation is that mild ozonolysis followed by scission of the ozonide reduces the molecular weight of polystyrene to the same order of magnitude as thermal degradation. In addition, the molecular weight of thermally degraded polystyrene is not reduced further by ozonolysis. The following mechanism has been proposed by Grassie and Cameron for the scission of unsaturated structures.



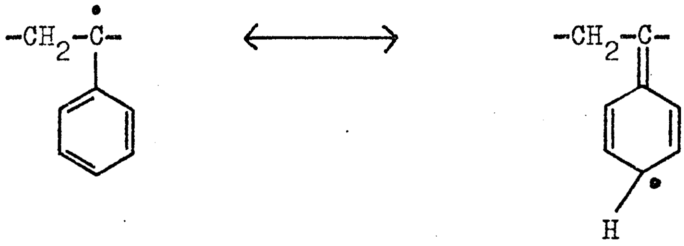
Using a computer programme, Wall[65] ignored 'weak link' scission and allowed for intermolecular and intramolecular transfer, but poor agreement was obtained between the theoretical and experimental results. However, Cameron and Kerr[66,67] have demonstrated that polystyrenes prepared using anionic initiators are free from 'weak links' and from further work on thermally initiated polystyrenes concluded that the labile structures are oxygenated groups, probably peroxide links which have become incorporated into the polymer during synthesis, but they were unable to prove this unequivocally. Unsaturated structures are unlikely to be the labile links as they calculated that the concentration of the 'weak links' is a factor of ten less than the concentration of the unsaturated structures.

1.4 Crosslinking of Polystyrene.

Polymerisation of monomers with a functionality greater than two or formation of crosslinks between preformed linear polymers are the two general methods employed in the synthesis of crosslinked polymers. These reactions are used to effect desired changes in the physical properties of polymers, the most useful being an increase in hardness and strength. The agencies by which crosslinking may be accomplished are heat, irradiation and chemical reaction with either a curing compound or a catalyst.

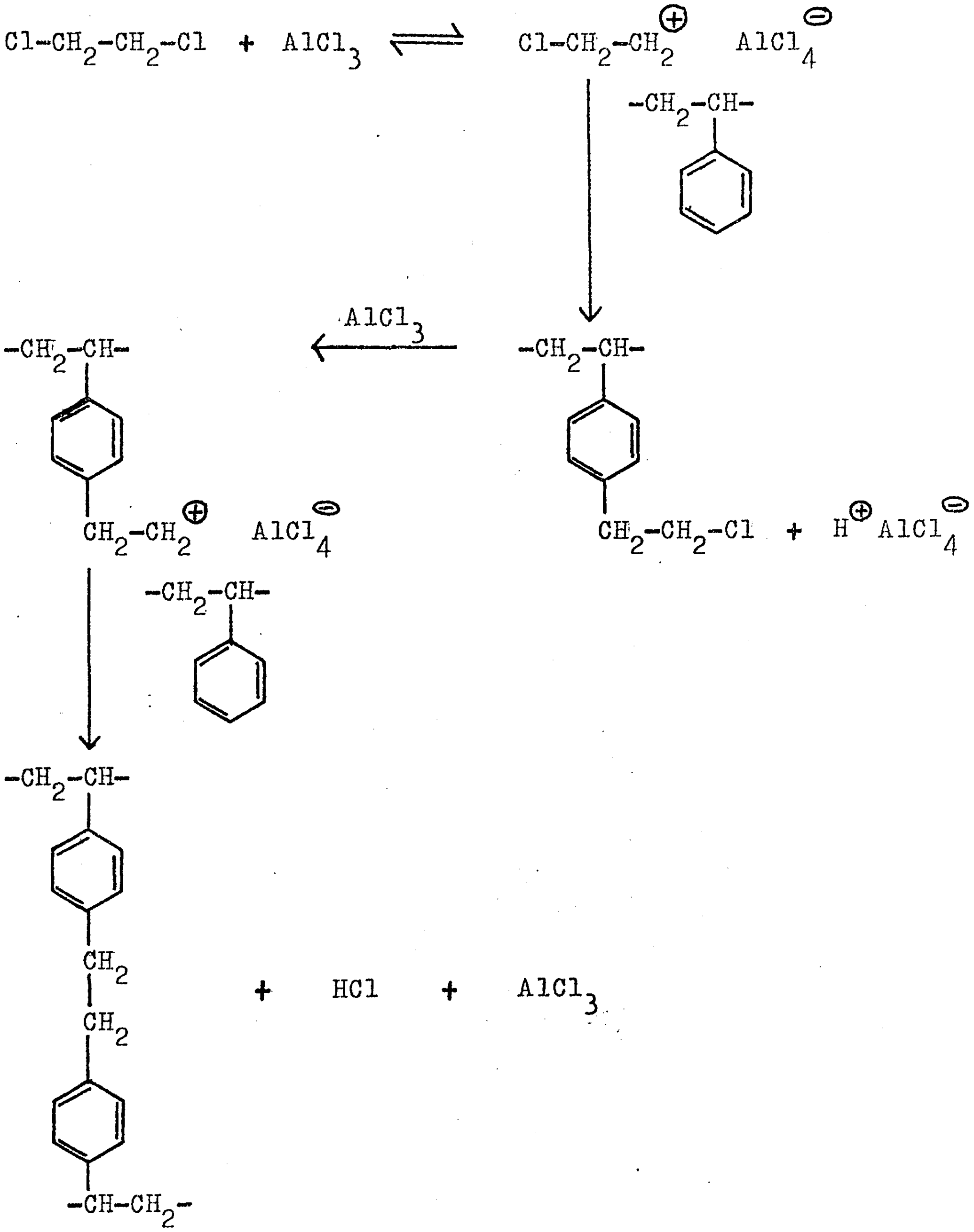
The theory of crosslinking linear polymer molecules to form an infinite three dimensional network has been developed mainly by Flory[68] and it has been demonstrated that by application of this theory, the degree of crosslinking of a polymer may be obtained from molecular weight measurements.[69,70] Although there may be intramolecular crosslinks which are ineffective in increasing the molecular weight, particularly approaching the gel point, relatively few crosslinks are required to gel a linear polymer. The onset of gelation during a crosslinking reaction marks the division of the solution into two distinct phases, namely, the gel which is insoluble due to the presence of infinitely high molecular weight species and the sol which is soluble and can be extracted from the gel since the polymer molecules present are still of relatively low molecular weight. As the polymerisation proceeds beyond the gel point, the quantity of the gel phase increases, the quantity of sol decreases and the mixture rapidly transforms from a viscous liquid to an elastic material of infinite viscosity.

Polystyrene crosslinks readily when exposed to ultra-violet radiation[71] due to the stability of the polystyryl radical formed by the cleavage of an α-hydrogen atom.

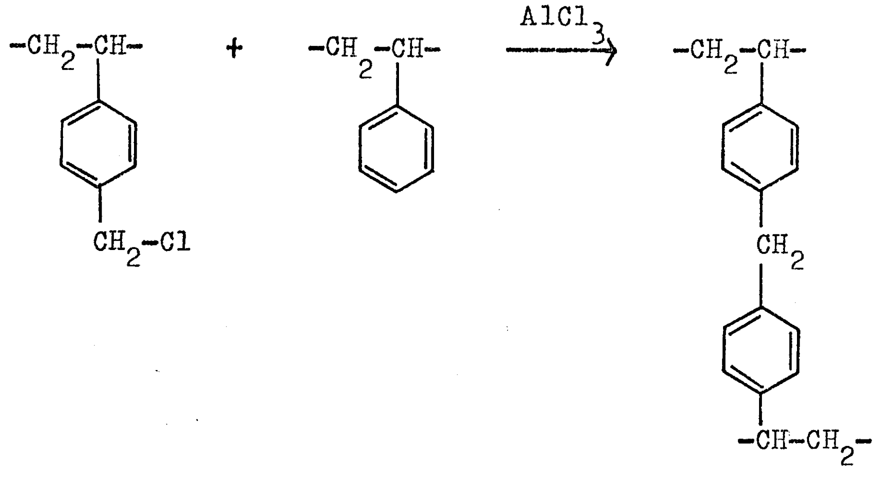


Combination between radicals of this type results in branched chains and eventually in a three dimensional network. Although these radicals should also be produced during the free-radical polymerisation of styrene, experimental determinations of transfer rate constants indicate that the extent of branching in free-radically initiated polystyrenes is very low even at high percentage conversions.

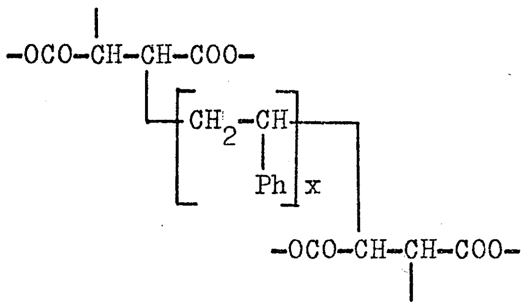
Crosslinking preformed linear polymers generally involves reactions which are completely different from those by which the polymers were synthesised originally. Bevington and Norrish[72] reported that no reaction occurred with a mixture of polystyrene and aluminium trichloride in nitrobenzene but that a Friedel-Crafts alkylation was observed when 1,2-dichloroethane was used as solvent.



This demonstrates that polystyrene may be readily crosslinked using Lewis acids and this has also been shown in the reaction between polystyrene and poly(p-vinyl benzyl chloride) in the presence of aluminium trichloride[73] by identification of the following reaction products.



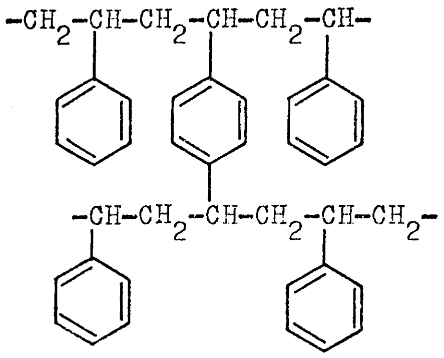
Polystyrene itself may also be employed as a curing agent and using this technique unsaturated polyesters are crosslinked with short, grafted polystyrene chains.



Trichain star polystyrenes, prepared by the condensation between polystyryl anions and 1,3,5-tri(chloromethyl)benzene have also been synthesised.[74] By this method the degree of branching can be controlled exactly and the effect of branching on the dilute solution behaviour of polymers may be investigated.

Thus it has been shown that crosslinked or branched polystyrenes may be formed by radical, cationic and anionic reactions involving reaction sites independent of those required for the formation of the linear polystyrene. However, the most common approach to the preparation of crosslinked polystyrene is the copolymerisation of styrene with p-divinyl benzene (D.V.B.). D.V.B. itself may be easily polymerised to yield brittle, insoluble resins which are commercially unsatisfactory. If D.V.B. is copolymerised in low concentration with styrene, the resultant crosslinked copolymers have the appearance of polystyrene, but possess higher heat distortion temperatures, greater hardness and strength and have better impact properties. Suspension polymerised beads of styrene/D.V.B. copolymers are employed as the basis for ion exchange resins, the ionic exchange sites being introduced later by substitution at the aromatic nuclei. The crosslinks in the bead structure help to stabilise them and minimise swelling. Ion exchange resins are the main commercial application of styrene/D.V.B. copolymers but D.V.B. is also employed in the production of styrene/butadiene rubbers.

A thorough study of the styrene/D.V.B. copolymerisation has been made by varying the comonomer ratio.[75] Both intermolecular and intramolecular crosslinks were considered to contribute to the formation of a three dimensional network, macrogelation being envisaged to occur by an accumulation of microgels formed by the intramolecular process. The type of crosslink formed is,



Copolymers of styrene and D.V.B. are employed as matrices for ion exchange resins because styrene monomer is cheap and plentiful, the copolymers have excellent physical strength and they are relatively resistant to degradation by oxidation, hydrolysis and elevated temperatures. Recently conventional styrene/D.V.B. copolymers have been modified to form macroreticular ion exchange resins, by incorporating linear polystyrene within the monomer phase during polymerisation.[76] The linear polystyrene can be removed easily by solvent extraction so that the resultant beads exhibit high porosity. A greatly increased rate of diffusion is, thus, obtained compared with the conventional gel type resins having the same degree of crosslinking.

As the glass transition temperature (T_g) of an amorphous polymer is related to the onset of segmental motion, crosslinking must increase the T_g due to the greater energy required for motion in the more rigid chains. The effect of D.V.B. on the T_g of styrene/D.V.B. copolymers has been determined[77] and may be expressed by the equation,

$$\Delta T_g = 5.86 \text{ (mole \% D.V.B.)}$$

which demonstrates that the increase in T_g is directly proportional to the quantity of D.V.B. present in the copolymer and thus to the degree of crosslinking.

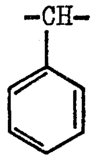
1.5 Friedel-Crafts Polymers.

In the presence of Friedel-Crafts catalysts, the polycondensation of benzyl compounds to yield macromolecular hydrocarbon materials is a flexible method for the formation of aromatic resins with specific structures and properties. Although the most thoroughly investigated monomer is benzyl chloride, benzyl halides, alcohols, ethers and aldehydes have been employed in the formation of polybenzyls. Either a soluble, low molecular weight material which softens at about 80°C or a granular solid which is infusible and insoluble may be produced by varying the reaction conditions and catalyst in the reactions involving benzyl compounds in the presence of Lewis acids.

Much controversy exists about the structure of polybenzyl and four possible structures have been proposed.

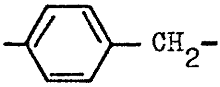
a) Polystilbene.

Henne and Leicester[78] proposed this structure but little supporting evidence has been obtained and it is generally not considered very probable.

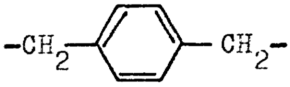


b) Linear.

This structure was first proposed by Jacobson,[2] who suggested that the benzene nuclei were predominantly disubstituted in the para position.



However, this type of polymer should be crystalline and high melting, similar to the poly(p-xylylene)s,



but polybenzyls do not possess these physical properties.

c) Random Branching.

Flory[79] has proposed that polybenzyl is an example of a polymer exhibiting random branching as shown in Figure 2. This type of structure would be formed if at any stage in the reaction, every hydrogen on any benzene nucleus has an identical probability of being substituted, subject to the directing influences of the existing substitution.

d) 'Sow and Piglet' Branching.

Based on infra-red, oxidative and degradative studies, Haas[5] has presented evidence for a structure consisting of a core of almost completely substituted benzene rings surrounded by a periphery of pendant benzyl groups as shown in Figure 3. This structure is supported by the spectroscopic and kinetic observations of Valentine and Winter[6].

Although it has been established that polybenzyl is predominantly composed of phenyl and phenylene groups linked by methylene bridges, some doubt still remains concerning the detailed structure. The majority of experimental evidence suggests that the structure proposed by Haas is the true representation, but the effect of steric crowding due to the adjacent benzyl groups appears to have been neglected. A more reasonable structure seems to be one in which the average degree of substitution, in all but the peripheral benzyl groups, is lower than that suggested by Haas. Parker[80] has proposed that a more reasonable value for the average degree of substitution is three and has suggested the structure shown in Figure 4. In addition, he has observed that the analytical results for the soluble and insoluble resins are virtually identical and hence deduced that the structures of both types of polybenzyl are similar.

A very flexible approach to the formation of aromatic resins

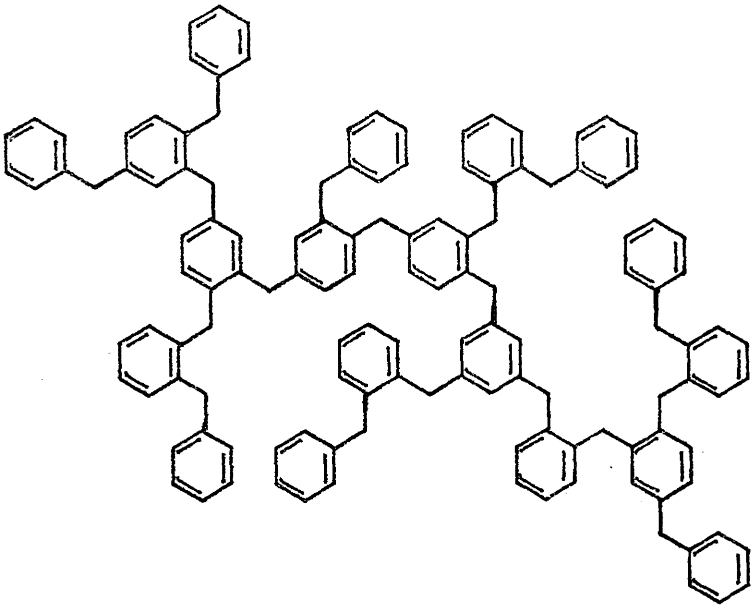


Figure 2.

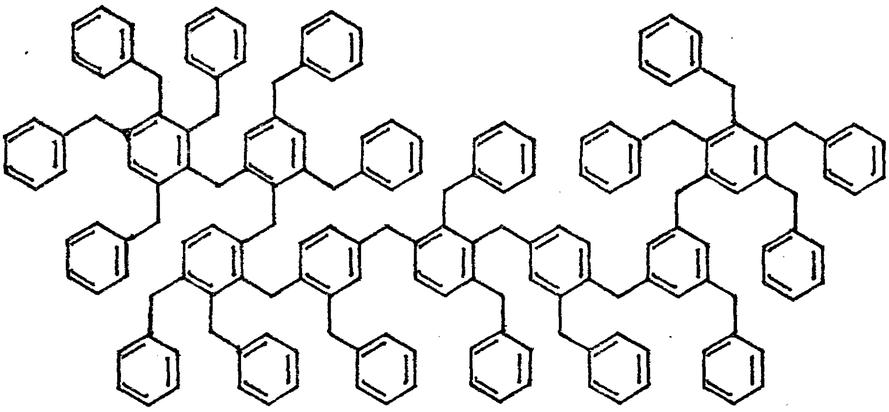


Figure 3.

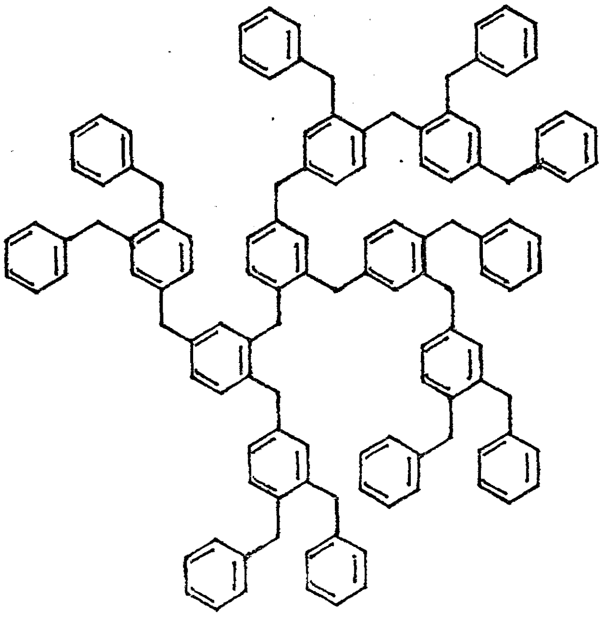


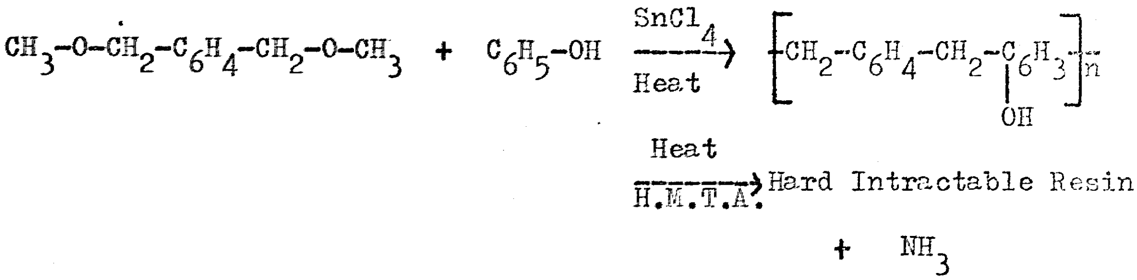
Figure 4.

involves the Friedel-Crafts condensation between an aromatic dichloromethyl compound and another aromatic compound. The condensation of p-di(chloromethyl)benzene (D.C.M.B.) and diphenyl ether in the presence of stannic chloride is a simple example of the use of this alkylation reaction in the synthesis of a prepolymer. Harris[14] has shown that additional heating effects the rapid curing of this prepolymer, by the D.C.M.B. already present, with evolution of HCl.

$$\begin{array}{lll} Cl{-}CH_2{-}C_6H_4{-}CH_2{-}Cl & \xrightarrow[\text{Heat}]{SnCl_4} & \left[C_6H_4{-}O{-}C_6H_4{-}CH_2{-}C_6H_4{-}CH_2\right]_n \\ + & & \\ C_6H_5{-}O{-}C_6H_5 & & \\ & \xrightarrow[\substack{\text{Heat} \\ \text{D.C.M.B.}}]{SnCl_4} & \text{Crosslinked Resin} + HCl \end{array}$$

Phillips[10] also discovered that D.C.M.B. may be employed as a coupling agent in the development of polybenzyl with useful properties. Overhults and Ketley[81] have used this type of condensation to investigate the effect of methyl substitution in the aromatic rings of polybenzyls. They demonstrated that by varying the number and position of the methyl substitutuents in the aromatic nuclei of the comonomers, both the melting point and crystallinity of the resultant polymer could be controlled.

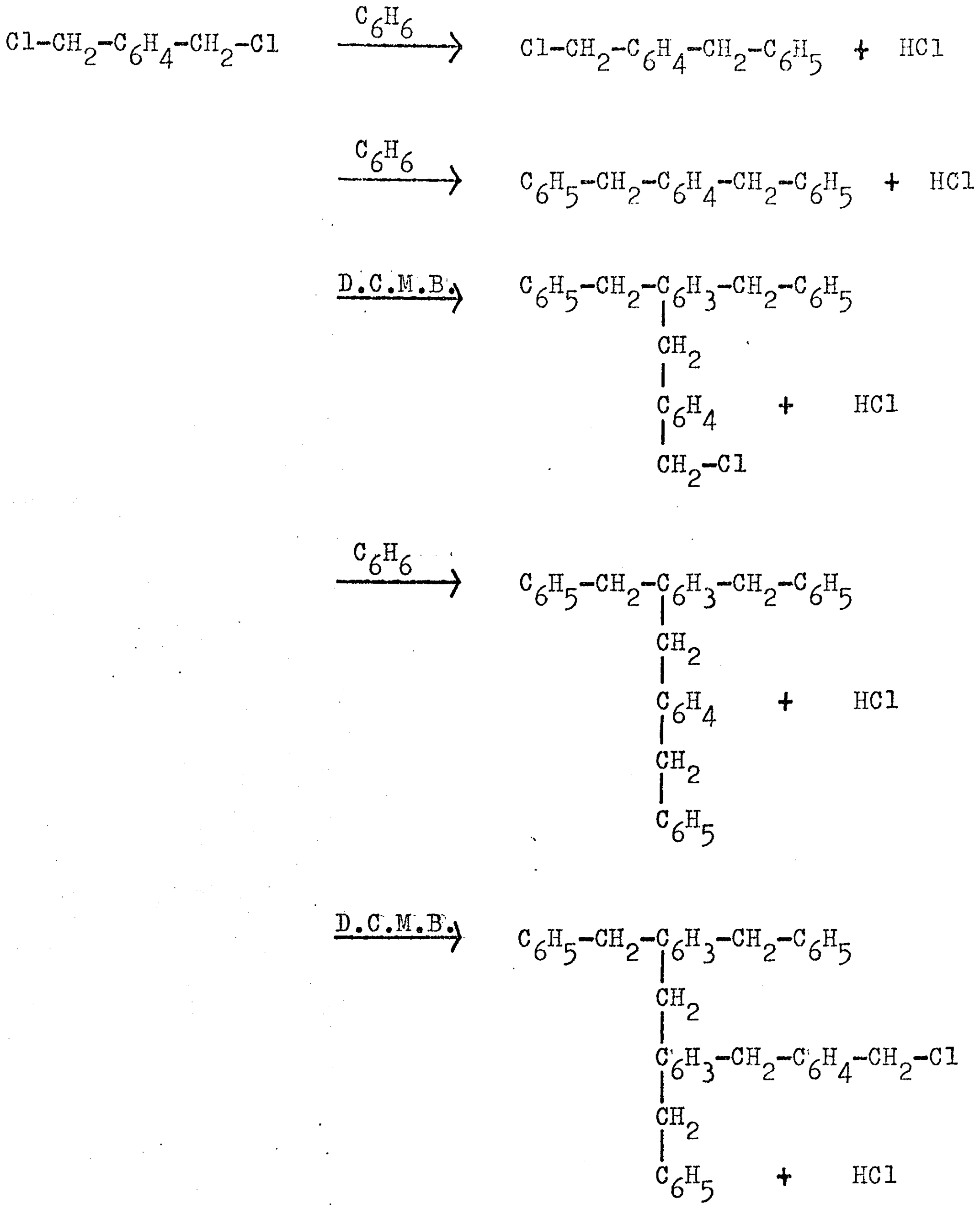
Crosslinked polymers of the above type, having great inertness and heat stability, high fibre adhesion and non-corrosiveness to metals are now being produced commercially by two distinct processes. In the first,[82] benzyl chloride is self-condensed in the presence of stannic chloride and then the prepolymer is cured in the presence of stannic chloride and dimethyl-p-xylenyl ether (D.M.X.E.), to yield a heat resistant polymer. The second[83] and more successful method involves heating a mixture of D.C.M.B. or D.M.X.E. and phenol, using stannic chloride as the catalyst. Following formation of the prepolymer, crosslinking is induced by hexamethylenetetramine (H.M.T.A.), which forms stable methylene linkages.



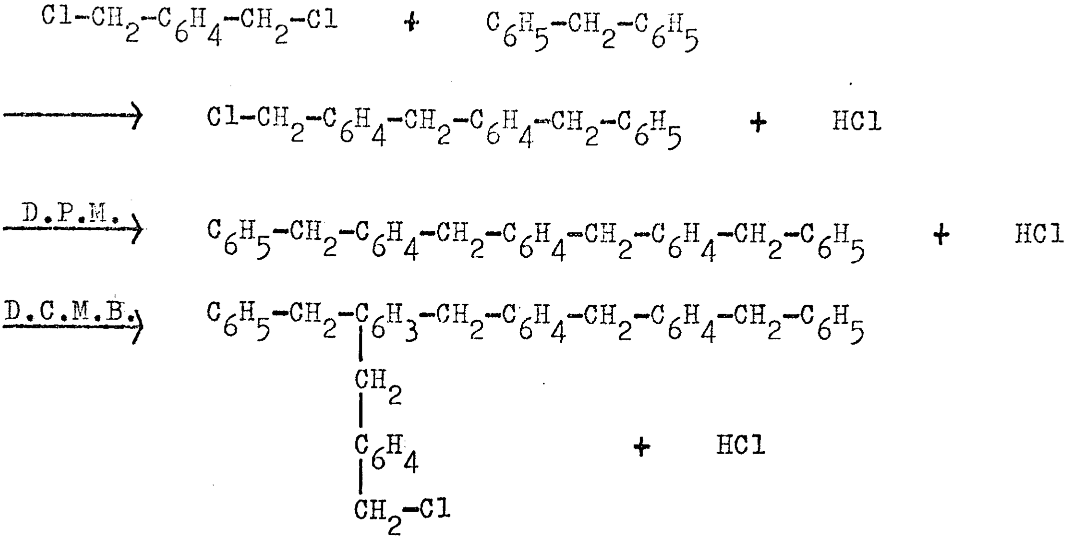
$$CH_3{-}O{-}CH_2{-}C_6H_4{-}CH_2{-}O{-}CH_3 + C_6H_5{-}OH \xrightarrow[\text{Heat}]{SnCl_4} \left[CH_2{-}C_6H_4{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{C_6H_3}} \right]_n \xrightarrow[\text{H.M.T.A.}]{\text{Heat}} \text{Hard Intractable Resin} + NH_3$$

In practice a mixture of substituted phenols is used to vary the properties of the products as is required.

Grassie and Meldrum[15-23] have demonstrated the versatility of Friedel-Crafts Polymers further with a detailed investigation of the products and kinetics of the condensation of benzene, diphenyl methane (D.P.M.) and benzyl chloride with D.C.M.B., using stannic chloride as the catalyst. Their results indicate that the frequency of branching in the polymer and hence both its thermal and physical properties can be greatly influenced by changes in the aromatic comonomer. Figures 5,6 and 7 illustrate the initial stages of the three reactions, respectively. The first two products of the reaction between benzene and D.C.M.B. must be linear but thereafter Grassie and Meldrum have shown that branching occurs at the earliest possible stage, due to the greater rate of substitution into disubstituted nuclei than into monosubstituted nuclei. It can be seen, therefore, that a highly branched structure will be formed preferably in the reaction between benzene and D.C.M.B., but a mixture of linear and branched chains



<u>Figure 5</u>. One Possible Reaction Sequence in the Benzene/D.C.M.B. Condensation.



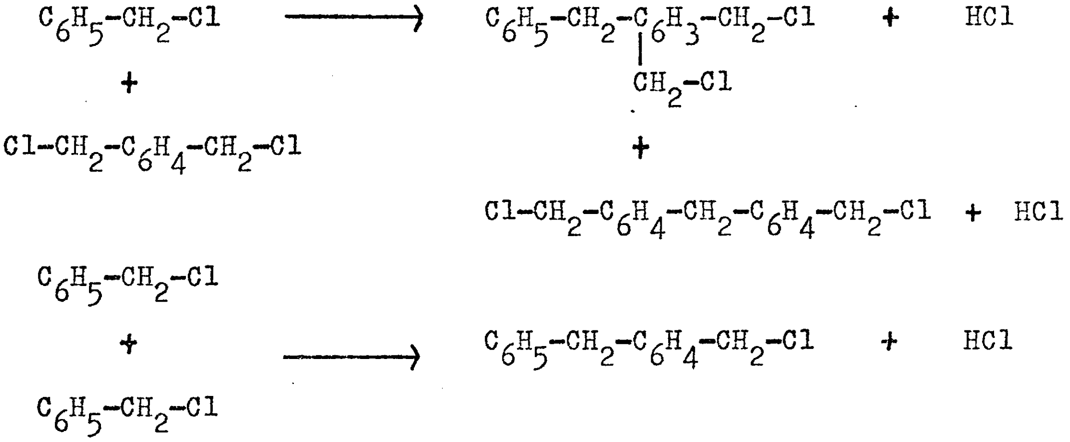
$$Cl{-}CH_2{-}C_6H_4{-}CH_2{-}Cl \quad + \quad C_6H_5{-}CH_2{-}C_6H_5$$

$$\longrightarrow \quad Cl{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_5 \quad + \quad HCl$$

$$\xrightarrow{D.P.M.} \quad C_6H_5{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_5 \quad + \quad HCl$$

$$\xrightarrow{D.C.M.B.} \quad C_6H_5{-}CH_2{-}\underset{\substack{|\\ CH_2\\ |\\ C_6H_4\\ |\\ CH_2{-}Cl}}{C_6H_3}{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_5 \quad + \quad HCl$$

Figure 6. One Possible Reaction Sequence in the D.P.M./D.C.M.B. Condensation.



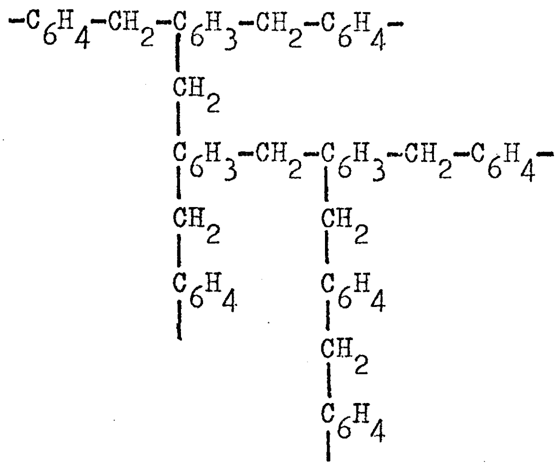
$$C_6H_5{-}CH_2{-}Cl + Cl{-}CH_2{-}C_6H_4{-}CH_2{-}Cl \longrightarrow C_6H_5{-}CH_2{-}\underset{\substack{|\\ CH_2{-}Cl}}{C_6H_3}{-}CH_2{-}Cl \quad + \quad HCl$$

$$+ \quad Cl{-}CH_2{-}C_6H_4{-}CH_2{-}C_6H_4{-}CH_2{-}Cl \quad + \quad HCl$$

$$C_6H_5{-}CH_2{-}Cl + C_6H_5{-}CH_2{-}Cl \longrightarrow C_6H_5{-}CH_2{-}C_6H_4{-}CH_2{-}Cl \quad + \quad HCl$$

Figure 7. Possible Initial Steps in the Benzyl Chloride/D.C.M.B. Condensation.

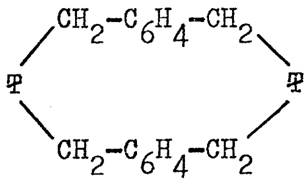
consisting of alternating methylene and benzenoid groups, which rapidly increases in complexity, is formed as the reaction progresses.



Further information concerning the products and kinetics of formation has been obtained by studying the condensation between D.P.M. and D.C.M.B., which yields less highly branched products, although they possess an identical basic methylene/phenylene structure. In this reaction the earliest possible stage at which branching can occur is after a linear product containing five aromatic nuclei is formed, and the subsequent branches also contain greater linearity. The products of the condensation between benzyl chloride and D.C.M.B. were found to be very complex due to the self-condensation of benzyl chloride which occurs in addition to the benzyl chloride/D.C.M.B. condensation. This made separation and identification of the products very difficult since rapid formation of extremely highly branched structures occurs in this system.

These investigations have demonstrated that by careful separation and analysis of the reaction products, the mechanism and kinetics of polymers of the polybenzyl type structure may be determined. The effect of changes in the nature and initial proportions of the reactants on the structure and properties of the products should, therefore, be capable of estimation.

The synthesis of polybenzyls containing heterocyclic units has also been achieved by Grassie and Meldrum, employing the reaction between aromatic heterocyclic compounds and D.C.M.B. Measurement of the relative thermal stabilities of these products by Thermal Volatilisation Analysis indicated that of the polymers prepared, the thiophene (Ψ)/D.C.M.B. polymer was thermally more stable than the benzene/D.C.M.B. polymer. For this reason, Grassie and Colford[24,25] investigated the kinetics and products of the Ψ/D.C.M.B. condensation, and their observations indicated that the chloromethyl groups react preferentially with the thiophene nuclei rather than with the benzene nuclei. This means that in the initial stages of the reaction the products will be much less branched than in the benzene reaction and the majority of branches formed in the later stages of the condensation will occur at the thiophene nuclei. Another basic structural difference compared with the benzene polymers is that intramolecular cyclisation occurs to form structures of the type,

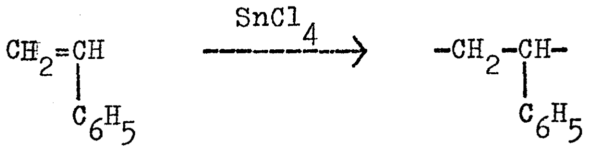


and incorporation of these structures into large, complex molecules will result, effectively, in a partial ladder structure, thereby accounting for the higher thermal stability of the thiophene/D.C.M.B. polymers.

1.6 Object of the Current Investigation.

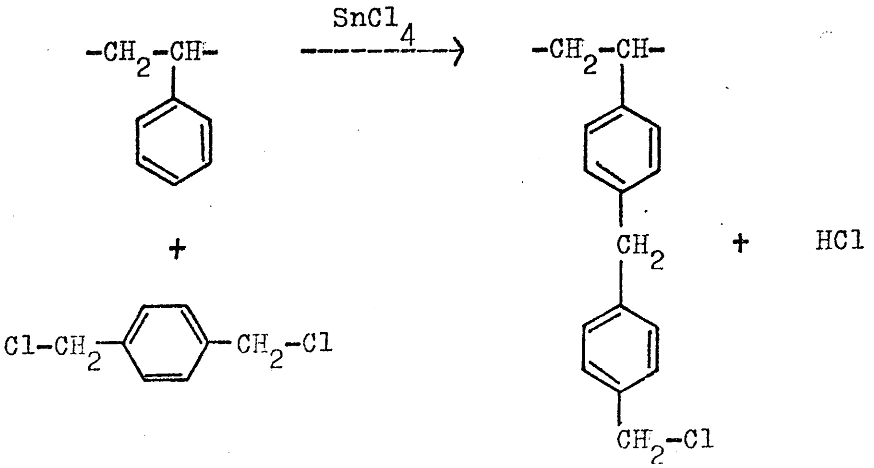
Following these investigations into Friedel-Crafts Polymers, the reaction between aromatic nuclei present in linear polymers and D.C.M.B. could prove a valuable method for the synthesis of crosslinked polymers. Friedel-Crafts alkylations between polystyrene and D.C.M.B. should provide a synthetic route to producing polystyrenes with more flexible crosslinks than those present in the rigid chains of styrene/D.V.B. copolymers. The aim of the present investigation, therefore, is to study the kinetics and mechanism of the crosslinking of polystyrene by D.C.M.B., using stannic chloride as the catalyst, in 1,2-dichloroethane solution. Since styrene may be polymerised by Friedel-Crafts catalysts, it should be possible to produce crosslinked polystyrene using a two stage process involving prepolymerisation and curing.

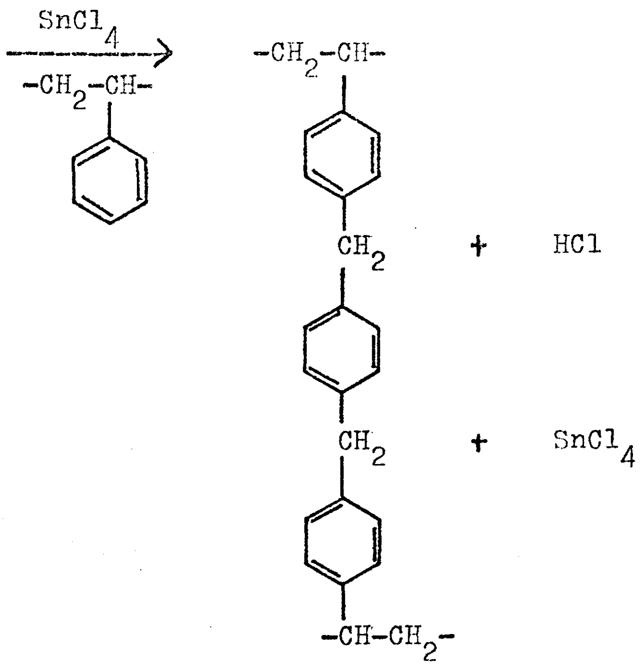
a) Prepolymerisation.



$$CH_2{=}CH(C_6H_5) \xrightarrow{SnCl_4} -CH_2-CH(C_6H_5)-$$

b) Curing.





The method should also be applicable for crosslinking copolymers containing small percentages of styrene.

CHAPTER TWO.

EXPERIMENTAL TECHNIQUES AND APPARATUS.

2.1 Manipulation of Reactants.

Accuracy is essential in kinetic experiments, and for this reason particular attention must be paid to the purity of the reactants. This section, therefore, describes the rigorous procedures which were employed to ensure the degree of reproducibility required.

Since traces of water and other impurities, especially residual drying agents, are known to have a profound effect upon catalysed reactions of the type being studied, strict precautions must be taken to minimise contamination. All reagents were purified and dried using, wherever possible, all glass apparatus with break seals instead of stopcocks, in order to prevent contamination by vacuum grease which can easily be 'carried' during a distillation. Pyrex glassware, which was used throughout, was washed and dried thoroughly before use and was always flamed out at a pressure of less than 10^{-4} torr immediately before sealing off. The purity of all the reactants, except polystyrene and stannic chloride, was checked by Gas Chromatography.

a) Purification of p-Di(chloromethyl)benzene.

p-Di(chloromethyl)benzene (D.C.M.B.) (Bush, Boake and Allen Ltd.) was recrystallised from methanol (B.D.H. Ltd., Analar Grade) until a constant melting point (99°C) was obtained. This white crystalline solid was dried in a vacuum oven at 60°C for 24 hours to ensure the complete removal of solvent residues.

b) Purification of Styrene.

Preliminary drying of styrene (Forth Chemicals Ltd.) was carried out by storing over calcium hydride at atmospheric pressure, at 0°C, for one week. After filtering, the partially dried styrene was degassed several times, by the freezing and thawing method, and distilled under vacuum on to finely divided calcium hydride in a storage ampoule, shown in Figure 8. The ampoule was then sealed off under vacuum at constriction A, at a pressure of less than 10^{-4} torr, and stored for a period of at least one week at a temperature of 0°C, during which time it was intermittently agitated. Drying was completed using the apparatus shown in Figure 9 in which B is the storage ampoule described in Figure 8. The apparatus was evacuated and sealed off at constriction C. Break seal D was then broken using a magnetic stirrer encased in glass and the styrene was distilled into a storage ampoule E, which was then sealed off at constriction F. As purification could not be improved by further drying or distillation, the styrene was stored in the storage ampoule E, under high vacuum at 0°C, until required. Storage at 0°C was necessary to prevent polymerisation, since the inhibitor, p-tert butyl catechol had been removed in the distillation.

c) Purification of Toluene.

Toluene (B.D.H. Ltd., Analar Grade) was purified using exactly the same procedure as for styrene, except that it was finally stored at room temperature.

d) Purification of Stannic Chloride.

Phosphorus pentoxide was added to G in Figure 10 via the aperture I which was then sealed off under atmospheric pressure. The apparatus was then evacuated, and the phosphorus pentoxide purified by

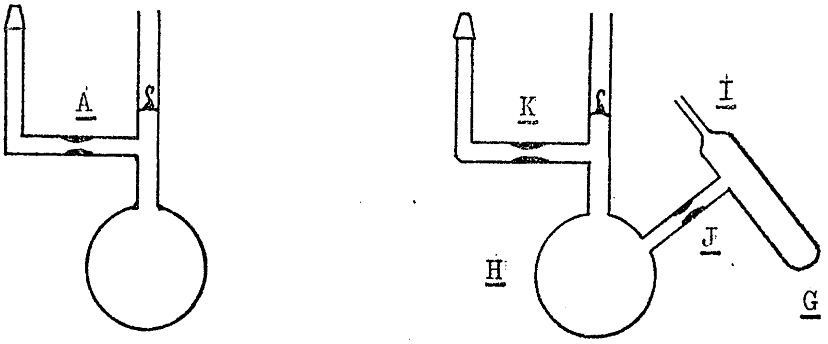


Figure 8. Figure 10.

Figures 8 and 10. Typical All-Glass Ampoules.

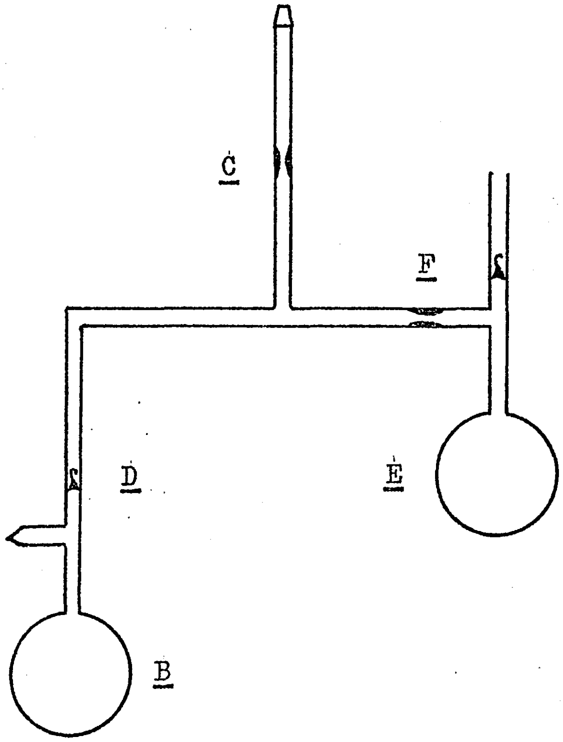


Figure 9. Greaseless Distillation Apparatus.

sublimation into H. The ampoule was finally sealed off at J.

Stannic chloride (Anhydrous, B.D.H. Ltd., Reagent Grade) was quickly transferred from its sealed container to a reservoir which was then attached to the vacuum apparatus and evacuated. The stannic chloride was degassed several times and distilled under vacuum on to the freshly sublimed phosphorus pentoxide in the drying ampoule H. After sealing off the drying ampoule at constriction K, at a pressure of less than 10^{-4} torr, the contents were stored for at least one week in the dark. Following this drying procedure the stannic chloride was distilled under high vacuum into a storage ampoule using apparatus similar to that described in Figure 9, except that storage ampoule B has been replaced by drying ampoule H. Using similar all glass apparatus, the stannic chloride was redistilled to ensure that all traces of dissolved phosphorus pentoxide had been removed. Stannic chloride was stored in the dark at all times, when not in use, to prevent radical decomposition by light.

e) Purification of 1,2-Dichloroethane.

1,2-Dichloroethane (D.C.E.) (B.D.H. Ltd., Reagent Grade) was pre-dried over phosphorus pentoxide at atmospheric pressure for at least one week. The D.C.E. was then filtered into a reservoir and purified and dried using exactly the same techniques as those used for stannic chloride. It was not necessary, however, to store D.C.E. in the dark.

f) Purification of p-Methyl Benzyl Chloride.

p-Methyl benzyl chloride (M.B.C.) (Emanuel Ltd.) was purified and dried using exactly the same procedure as for D.C.E., except that the pure, dry M.B.C. was stored at $0^{\circ}C$ to prevent self-condensation. Great difficulty was encountered during distillation of the M.B.C.

owing to its high vapour pressure.

2.2 Preparation of Standard Solutions.

As only small quantities of stannic chloride were required, the following method using standard solutions of stannic chloride in D.C.E. was devised to allow reproducible introduction of small amounts of stannic chloride into the reaction ampoules. In all series of reactions except those involving toluene, the concentration of the standard solution was 0.0868 mole/l. (described below) and in the case of the toluene experiments the standard solution had a concentration of 0.434 mole/l.

The apparatus shown in Figure 11 was evacuated and sealed off at constriction L. After breaking the break seal M, 1 ml. of stannic chloride was poured from its storage ampoule N into the 1 ml. graduated ampoule O which was then sealed off at constriction P. The remaining stannic chloride was then distilled into storage ampoule Q, sealed off at constriction R and stored in the dark until required.

Using an identical type of apparatus 99 ml. of D.C.E. were transferred into the 100 ml. graduated ampoule S and the remainder distilled into the storage ampoule T and stored for future use.

Having now obtained the required quantities of stannic chloride and D.C.E., these were distilled into storage ampoule U using the apparatus shown in Figure 12. After evacuation the apparatus was sealed off at constriction V, the break seals W and X were broken and the stannic chloride and D.C.E. were distilled from graduated ampoules O and S, respectively, into storage ampoule U which was finally sealed off at constriction Y.

In the interest of accuracy graduated ampoules were chosen so

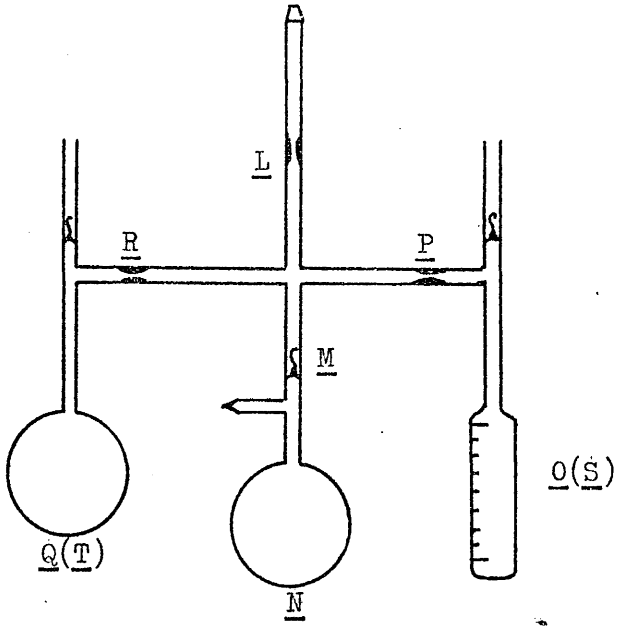


Figure 11. Greaseless Solution Transfer Apparatus.

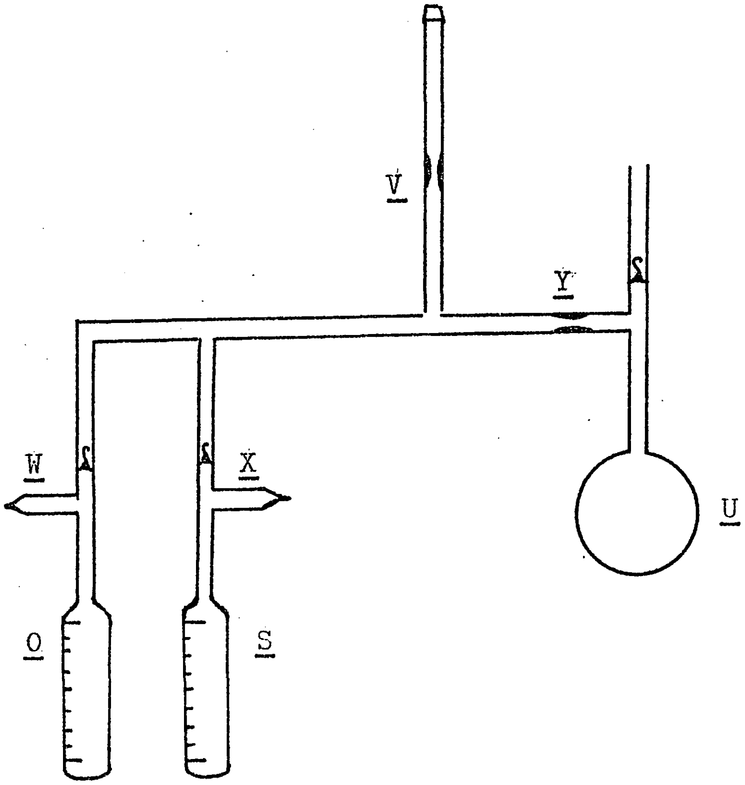


Figure 12. Greaseless Solution Transfer Apparatus.

that their volumes were as close to the required quantities as possible. The standard solution was now stored in the dark until required. It should be noted that at no time was the catalyst allowed to come into contact with any reagent other than solvent until commencement of a reaction was desired.

2.3 Preparation of Polystyrene.

Polystyrene was used as a reactant in a number of the series of experiments to be described in this thesis.

a) Polymerisation of Styrene.

24 ml. of styrene were transferred from its storage ampoule into a 50 ml. graduated ampoule and sealed off under high vacuum using apparatus identical to that shown in Figure 11. The remaining styrene was distilled into the storage ampoule, sealed off and stored at 0°C.

Using an identical procedure, 12 ml. of the standard stannic chloride solution were transferred to a 15 ml. graduated ampoule and the remaining standard stannic chloride solution transferred to the storage ampoule, both ampoules being sealed off under high vacuum at the appropriate times. It was necessary to pour the stannic chloride solution as stannic chloride and D.C.E. would not distill with equivalent velocities.

204 ml.of D.C.E. were transferred into a 250 ml. graduated ampoule under high vacuum from a storage ampoule using apparatus similar to that described in Figure 9. The graduated ampoule was sealed off but it was not necessary to retain the remaining D.C.E. as about 200 ml. is the maximum which can be handled practically.

Having now prepared the quantities of styrene, D.C.E. and standard stannic chloride solution desired for the polymerisation of styrene, the apparatus shown in Figure 13 was used to transfer the reactants into the reaction vessel. After evacuating, the apparatus was sealed off at constriction Z. Break seals a and b were broken and the styrene and D.C.E. were allowed to distil from graduated ampoules d and e respectively, into reaction vessel g. Once transfer of the styrene and D.C.E. was complete, break seal c was broken and the stannic chloride solution was allowed to distil from graduated ampoule f into reaction vessel g. Distillation of the stannic chloride solution was acceptable in this case since the entire contents of graduated ampoule f were being transferred. Since reaction vessel g was at -196°C during the distillation, as with all the distillations which have been and will be described, no catalysis can occur. Once the distillation of the stannic chloride solution was complete the reaction vessel was sealed off under high vacuum at constriction h.

The contents of reaction vessel g were thawed, mixed as quickly as possible and the reaction vessel was immersed in a stirred, thermostatically controlled water bath at 30 ± 0.5°C for 30 minutes. The reaction vessel was then opened and the contents precipitated by pouring slowly into 2.5 l. of methanol which was being stirred constantly. A fine, white precipitate of polystyrene was filtered, washed several times with methanol and dried in a vacuum oven at 60°C for 24 hours. The polystyrene was then redissolved in 250 ml. of 1-4 dioxan (B.D.H. Ltd., Analar Grade), reprecipitated into methanol, filtered, washed and dried as before. By weighing the polystyrene obtained it was found that approximately 40 % polymerisation had occurred.

This procedure was repeated five times to obtain sufficient polystyrene to perform all the desired reactions. Once they had been

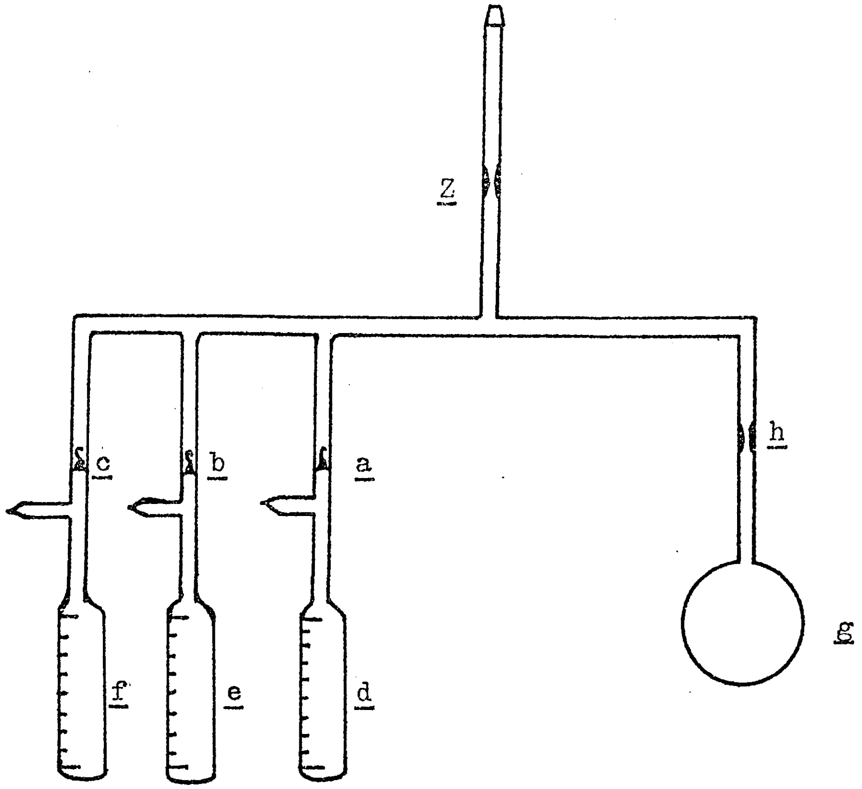


Figure 13. Greaseless Solution Transfer Apparatus.

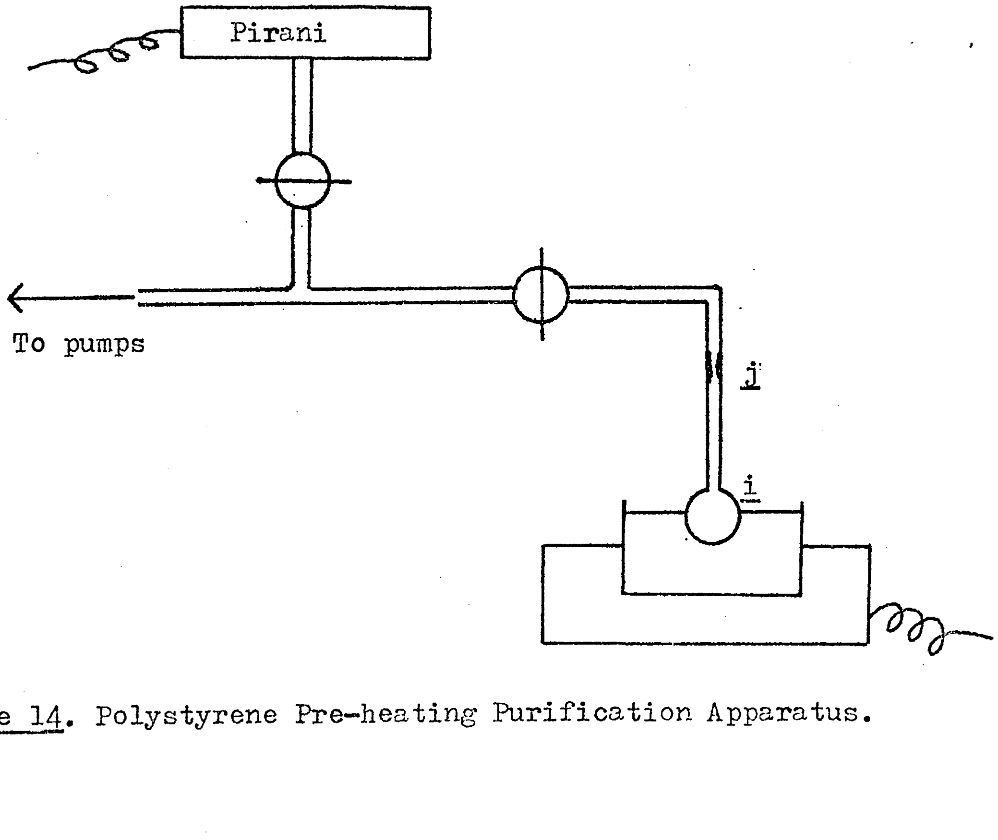


Figure 14. Polystyrene Pre-heating Purification Apparatus.

prepared, all six samples were dissolved in dioxan, the solutions combined and reprecipitated, filtered, washed and dried as described previously.

b) Purification of Polystyrene.

Analysis of the 'purified' polystyrene by infra-red and Thermal Volatilisation Analysis showed that it contained residual, trapped dioxan and, as it is known that stannic chloride forms complexes with ethers, removal of the occluded dioxan became necessary.

The apparatus shown in Figure 14 was devised to eliminate the dioxan from the polystyrene. The quantity of polystyrene required for a reaction was weighed into reaction vessel i, which was then attached to the vacuum apparatus. After evacuation of the apparatus, the reaction vessel containing the polystyrene was heated, using a silicone oil bath and electric heating mantle, to 180°C for 45 minutes.[84] A pirani gauge was used to follow the evolution of the dioxan from the polystyrene. When all the dioxan was removed, the reaction vessel was sealed off under high vacuum at constriction j and the polystyrene stored under high vacuum until required. Analysis of the pre-heated polystyrene showed no occluded compounds were present.

2.4 Condensation Reaction Procedure.

Four distinct condensation reactions have been studied and in order that full kinetic data might be obtained, each reaction was studied for varying times at various concentrations of all three reactants. For each type of reaction only one set of reactant concentrations has been chosen, at this stage, to illustrate the procedure. The procedure described here allows for the preparation of five identical solutions, simultaneously.

a) Styrene/D.C.M.B. Condensation.

5 ml. of styrene were transferred into a 5 ml. graduated ampoule, the remaining styrene being distilled into the storage ampoule, under high vacuum, using apparatus similar to that shown in Figure 11. Using an identical procedure, 2.5 ml. of standard stannic chloride solution and 42.5 ml. of D.C.E. were isolated from their main batches, under high vacuum, in 5 ml. and 50 ml. graduated ampoules, respectively. The standard solution of stannic chloride in D.C.E. was always shaken vigorously before use and in transfer reactions of all types involving styrene, speed is essential to reduce the possibility of unwanted polymerisation. The apparatus shown in Figure 15 was now employed to distribute the standard stannic chloride solution from its present position in graduated ampoule k into each of the five 1 ml. graduated ampoules l, on the periphery of the central reservoir m. The apparatus was evacuated, sealed off at constriction n, break seal o was broken and the standard stannic chloride solution transferred to the central reservoir m. 0.5 ml. of the stannic chloride solution was then introduced into each graduated ampoule l which was then sealed off at constriction p. 1 ml. of styrene and 8.5 ml. of D.C.E. were introduced into five 1 ml. and five 10 ml. graduated ampoules, respectively, by an identical procedure.

The apparatus shown in Figure 13 was now constructed with graduated ampoules containing the above quantities of styrene, D.C.E. and stannic chloride in positions d, e and f, respectively. 0.5 g. of D.C.M.B. was weighed into reaction vessel g which was then attached at point h. Following evacuation, the apparatus was sealed off at constriction Z and after breaking break seals a and b, the styrene and D.C.E. distilled on to the D.C.M.B. Once distillation was complete,

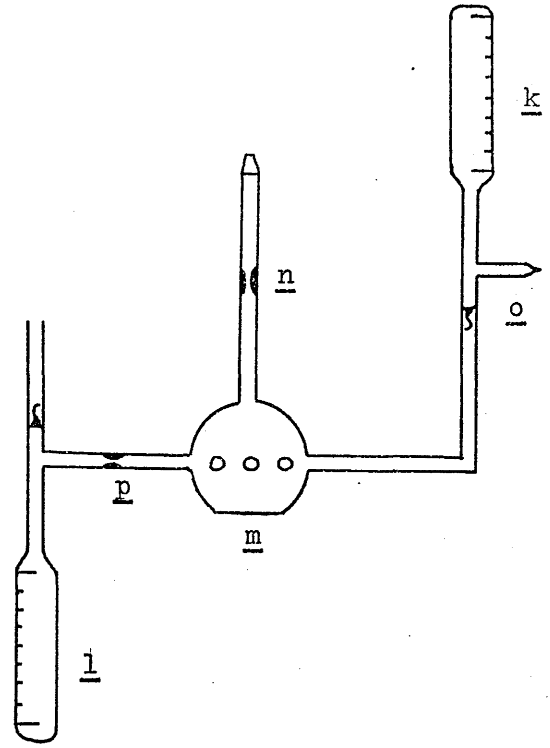


Figure 15. Greaseless Solution Distribution Apparatus.

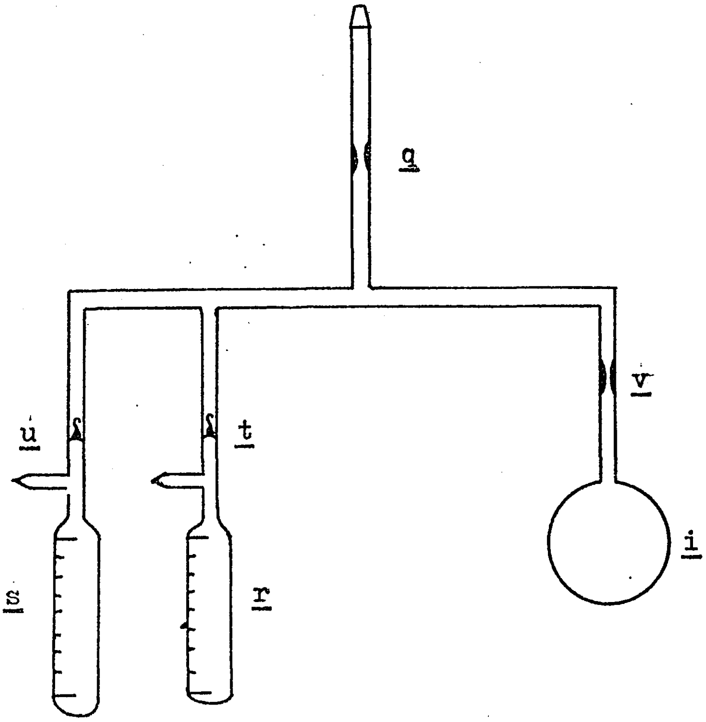


Figure 16. Greaseless Solution Transfer Apparatus.

break seal c was broken and the stannic chloride solution was allowed to distil into reaction vessel g. When this distillation was complete, the reaction vessel was sealed off at constriction h and kept at -196°C until required. Thus, by using this technique, five identical solutions of reactants were formed, the quantities being designed here, as in all other cases, so that the total reaction volume was 10 ml.

Each reaction vessel was then thawed, mixed as quickly as possible and immersed in a stirred, thermostatically controlled water bath at 30 ± 0.5°C for a predetermined time, after which the reaction vessel was opened and the contents precipitated and purified in an identical manner to that already described in the preparation of polystyrene.

b) Polystyrene/D.C.M.B. Condensation.

Stannic chloride solution was transferred from its storage ampoule and distributed into five 0.5 ml. portions in 1 ml. graduated ampoules as described in the previous section and D.C.E. was similarly transferred and distributed into five 9.5 ml. portions contained in 10 ml. graduated ampoules. For this reaction, the apparatus shown in Figure 16, in which r and s contained the D.C.E. and stannic chloride solution respectively, was used. 0.5 g. of D.C.M.B. was weighed into each reaction vessel i which contained 1.0 g. of pre-heated polystyrene and this was then attached to the apparatus at point v. The apparatus was evacuated and sealed off at constriction q and after breaking break seal t, the D.C.E. was allowed to distil on to the polystyrene and D.C.M.B. in reaction vessel i. Once distillation was complete, the reaction vessel contents were allowed to thaw and left until the polystyrene which, due to pre-heating, was solid and not a powder as before, had dissolved. The reaction vessel was then refrozen, break seal u broken and the stannic chloride solution allowed to distil into the reaction vessel. On completion of distillation, the reaction vessel was sealed off at constriction v. An identical procedure was used for all five reactions.

The contents of each reaction vessel were thawed, mixed and allowed to react as in the styrene/D.C.M.B. condensation. After a predetermined time, reaction was terminated and the reaction products purified as described in the synthesis of polystyrene.

c) Polystyrene/M.B.C. Condensation.

By employing a procedure identical to that used in the styrene/D.C.M.B. condensation, five 1 ml. graduated ampoules containing 0.5 ml. of M.B.C., five 1 ml. graduated ampoules containing 0.5 ml. of stannic chloride solution and five 10 ml. graduated ampoules containing 9.5 ml. of D.C.E. were prepared.

On this occasion, the apparatus used to fill the reaction vessels was that shown in Figure 17. 1.0 g. of pre-heated polystyrene in reaction vessel i was attached at point 7, the apparatus was evacuated and sealed off at constriction 8. Break seal 1 was broken and the D.C.E. was allowed to distil from graduated ampoule 10 into the reaction vessel. The contents of the reaction vessel were allowed to thaw, the polystyrene allowed to dissolve and then the contents were refrozen. Break seal 2 was now broken and the M.B.C. allowed to distil into the reaction vessel. The polystyrene was not allowed to dissolve in the presence of the M.B.C., which has a much higher reactivity than D.C.M.B. On the completion of distillation, the stannic chloride solution was allowed to distil through break seal 6 and finally the reaction vessel i was sealed off, under high vacuum, at constriction 9. Again a similar procedure was employed for all five reactions.

In these reactions, as before, condensation was allowed to

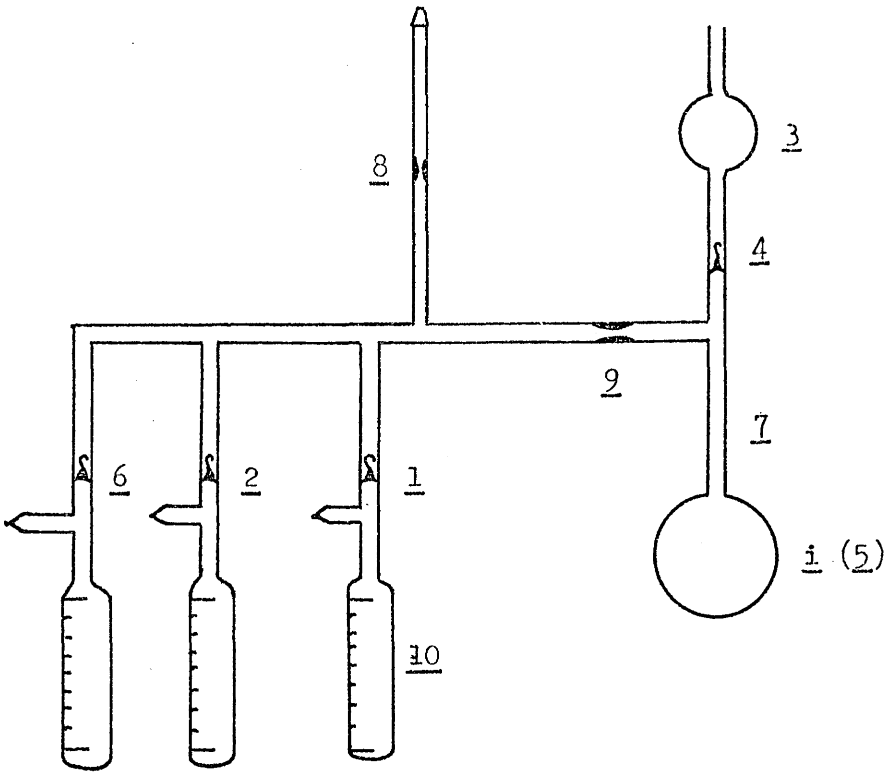


Figure 17. Greaseless Solution Transfer and HCl Estimation Apparatus.

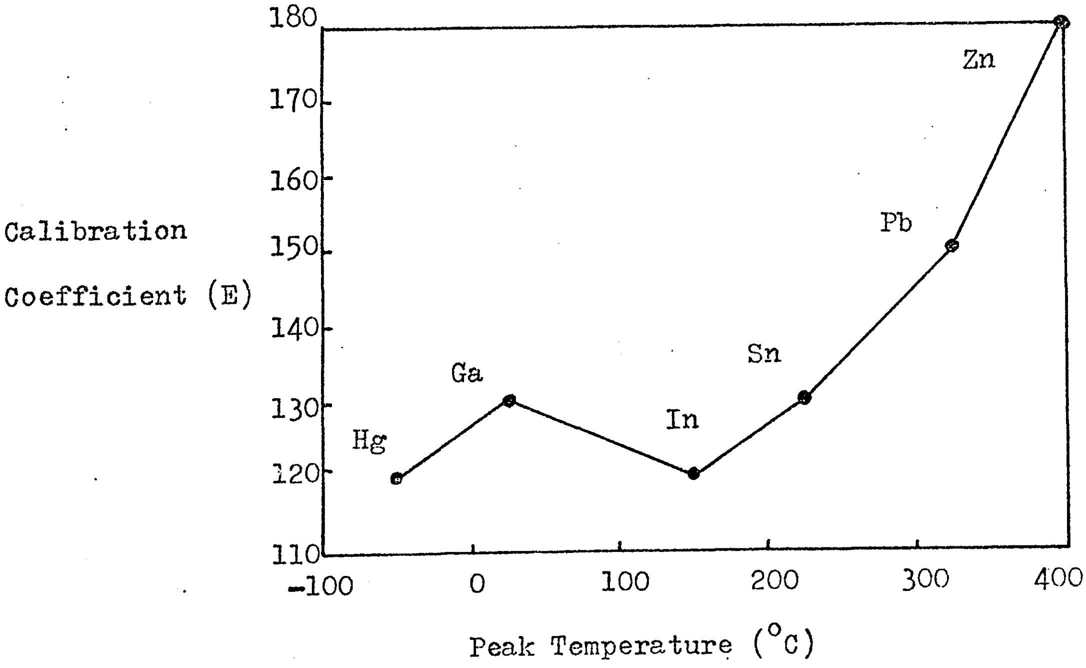


Figure 18. Relationship between Calibration Coefficient and Peak Temperature measured by D.S.C.

proceed at 30°C and terminated by the addition of distilled water from reservoir 3, via break seal 4 which was broken by a glass rod. The water and reactants were shaken vigorously, poured into a conical flask, the reaction vessel was washed out thoroughly and the washings added to the flask. The contents of the flask were then titrated with 0.1 N sodium hydroxide solution using p-nitrophenol as an indicator, in order to determine the quantity of HCl evolved during the reaction.

d) Toluene/D.C.M.B. Condensation.

1.0 g. of D.C.M.B. was weighed into an empty reaction vessel 5 which was then attached to the apparatus shown in Figure 17, at point 7. Five 1.0 ml. graduated ampoules containing 1.0 ml. of toluene, five 1.0 ml. graduated ampoules containing 0.5 ml. of stannic chloride solution and five 10 ml. graduated ampoules containing 8.5 ml. of D.C.E. were obtained by the method described for the styrene/D.C.M.B. reaction. The apparatus was evacuated and sealed off at constriction 8, the toluene and D.C.E. distilled into the reaction vessel by breaking break seals 1 and 2 respectively, and when distillation was complete, break seal 6 was broken and the stannic chloride solution allowed to distil into reaction vessel 5, which was then sealed off at constriction 9, under high vacuum.

The contents of all five reaction vessels were allowed to react at 30°C for predetermined times and the condensations terminated by distilled water as in the polystyrene/M.B.C. reaction. Again the HCl evolved was titrated but in addition, the organic layer was extracted with D.C.E., washed with distilled water, dried over anhydrous sodium sulphate, filtered and the D.C.E. allowed to evaporate, leaving the reaction products.

2.5 Spectroscopic Analysis.

a) Infra-red.

Using the KBr disc technique, infra-red spectra of the polymers were recorded on a Perkin-Elmer 225 Grating Infra-red Spectrophotometer, whereas the spectra of the products obtained from thermal degradative studies, whether solid, liquid or gaseous were recorded on a Perkin-Elmer 257 Grating Infra-red Spectrophotometer using NaCl plates.

b) Ultra-violet.

A Unicam S.P. 800 Ultra-violet Spectrophotometer was used to record ultra-violet and visible spectra of the polymers. Quantitative measurements were made using a 0.1% solution of a polymer in chloroform (B.D.H. Ltd., Analar Grade) in 5mm. quartz cells.

c) Nuclear Magnetic Resonance.

N.M.R. Spectra were obtained on a Perkin-Elmer R.10 60 Mc/s Spectrometer, in deutero-chloroform solution.

2.6 Molecular Weight Measurements.

The basic equation relating osmotic pressure (π) to number average molecular weight ($\overline{M}_n$) is the van't Hoff expression,

$$\pi = \frac{RTc}{\overline{M}_n}$$

where R and T have the usual significance and c is the concentration of the polymer solution in g./100g.

Molecular weights were obtained by measuring the osmotic pressure of solutions of the polymers at different concentrations and by plotting $\frac{\pi}{c}$ versus c. The straight line obtained was extrapolated to find $\left(\frac{\pi}{c}\right)_0$, the value of $\frac{\pi}{c}$ when $c=0$ (at infinite dilution). A simple conversion factor,[85] $\frac{2.53 \times 10^5}{\left(\frac{\pi}{c}\right)_0}$ gives $\overline{M}_n$ directly.

$\overline{M}_n$ may be represented by,

$$\overline{M}_n = \frac{\sum^{i} M_i N_i}{\sum^{i} N_i}$$

where N_i is the number of molecules of molecular weight M_i.

Molecular weights were measured on a Hewlett-Packard 501 High Speed Membrane Osmometer with Cellophane 300 membranes at 25°C. For molecular weights between 1,000,000 and 20,000 a 1% solution of polymer in toluene was used and for the measurement of molecular weights between 20,000 and 5,000 a 0.2% solution of polymer in toluene was used.

2.7 Thermal Methods of Analysis.

a) Differential Thermal Analysis. (D.T.A.)

In this technique[86] a sample and inert reference are heated or cooled at a known, fixed rate. The sample temperature is continously compared with that of the reference material, their temperature difference, ΔT, being plotted continuously as a function of the furnace temperature, T.

The D.T.A. module fitted to the Du Pont 900 Thermal Analyzer consists of a furnace or heating block into which two glass tubes containing the sample and reference, respectively, are placed. Thermocouples are inserted into the sample and reference and the whole assembly is covered by a bell jar to permit a controlled atmosphere.

This method of analysis is extremely sensitive and so that meaningful comparisons can be made between samples, such factors as sample size, consistency of packing, heating rate, atmosphere and thermocouple position must be reproducible.

All samples were analysed in a very finely divided state since thermal conductivity is being measured, under an atmosphere of nitrogen, at a heating rate of 10°C/min. and the sample size was 10mg.

b) Differential Scanning Calorimetry. (D.S.C.)

The D.S.C. technique is related to the D.T.A. method, the main practical difference being that the sample is enclosed in an aluminium pan and the reference is an empty pan. In theory D.S.C. should measure the differential energy required to maintain a sample and inert reference at the same temperature. This necessitates separate heaters for the sample and reference and a thermocouple circuit to signal an imbalance and increase the power to the sample during an endothermic transition or to the reference during an exothermic reaction. The area under the curve when heat change is plotted against temperature can be equated with the heat of reaction. The Du Pont 900 Thermal Analyzer fitted with the D.S.C. cell is not a true D.S.C. instrument as described above. In fact, it is a carefully designed D.T.A. cell which produces a differential temperature peak rather than a differential energy peak but heats of reaction can be obtained from the area under the curve with good calorimetric accuracy.

Calibration of the D.S.C. cell is achieved using known heats of fusion of metals and a calibration coefficient is obtained for the cell at the temperature at which the peak occurs for each metal using the equation,

$$E = \frac{\Delta HWa}{A\,\Delta TT}$$

where E is the calibration coefficient,

ΔH is the heat of reaction (cal/g.),

a is the heating rate (^{o}C/min.),

T is the X-axis scale (^{o}C/in.),

ΔT is the Y-axis scale (^{o}C/in.),

A is the area of the peak (sq. in.),

W is the sample size (g.).

Once E has been determined for that series of temperatures, a graph of E versus T, as shown in Figure 18, enables the calibration coefficient to be obtained for the temperature at which the peak of interest occurs. Knowing E, and rearranging the equation, unknown heats of reaction are easily obtained from the peak area.

Again so that comparisons could be made between samples, 10mg. samples, closely packed in flat pans were always heated in a nitrogen atmosphere at $10^{o}C$/min.

c) Thermogravimetric Analysis. (T.G.A.)

Thermogravimetry is used to study the weight loss of a material as a function of time in an isothermal operation or as a function of temperature in a linear temperature programmed operation. In this study, weight loss is only studied as a function of a fixed heating rate.

The Du Pont 950 Thermogravimetric Analyzer employs a null type balance in which any weight change in the sample is opposed by an equal restoring force applied to the beam. This restoring force is then a measure of the change in the weight of the sample. The 0.5kw. furnace is capable of operation up to $1200^{o}C$ and the curve of weight loss versus sample temperature is plotted on an X-Y recorder.

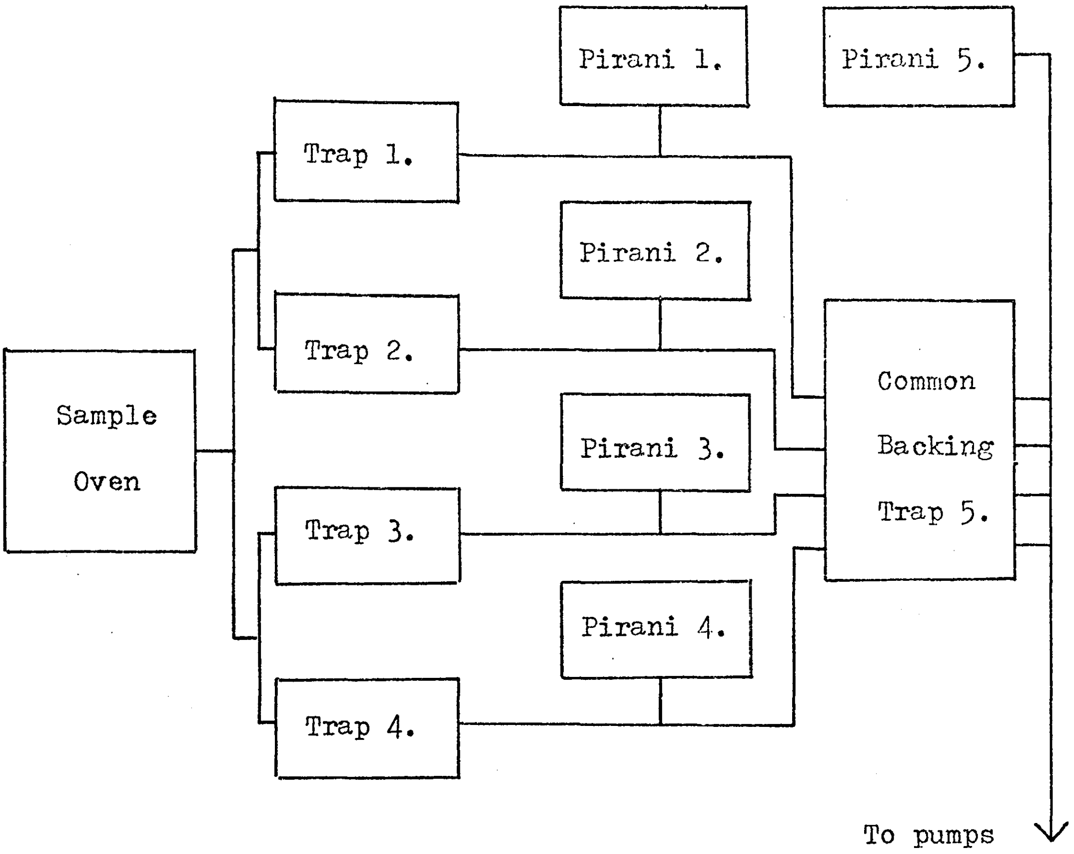
As before a heating rate of $10^{o}C$/min. was used to heat a 10mg.

sample in a platinum pan, in an atmosphere of nitrogen. Packing was necessarily loose in this case, as the pan is suspended very delicately and the thermocouple is not in the sample but extremely close to the outside of the pan.

d) Thermal Volatilisation Analysis. (T.V.A.)

This technique was devised by McNeill[87] and measures the thermal conductivity of the volatile material evolved from a heated polymer sample which is being continuously pumped. The differential condensation T.V.A. apparatus (D.C.T.V.A.) shown in Figure 19 was later developed by McNeill[88] and is a modification of the original equipment which employs a series of five traps maintained at different temperatures. After each trap is placed a Pirani gauge which measures the transient pressure of a material not condensed by that particular trap. The responses from the Pirani gauges are fed into a multi-point recorder so that they are recorded simultaneously. These traces of the responses are a measure of the rate of volatilisation against time. Each trace obtained gives an indication of the volatilities of the various products as well as the temperature at which they are produced. It has been found that polymers give very characteristic curves and much information about stability, reaction mechanisms and the nature of the volatile products can be deduced. Also, further information about the products can be obtained by analysis of the volatile materials which have condensed in the various traps, the short chain fragments which condense on the walls of the reaction tube outside the furnace and the residue.

A separate temperature versus time trace is also recorded so that when a linear temperature programme is used, as in normal practice, any deviations of the heating rate from linearity may be checked. As



Normal Working Temperatures:

Trap 1.	-100°C
Trap 2.	-75°C
Trap 3.	-45°C
Trap 4.	0°C
Trap 5.	-196°C

<u>Figure 19</u>. Schematic Diagram of the Differential Condensation Thermal Volatilisation Analysis Apparatus. (D.C.T.V.A.)

T.V.A. is carried out under high vacuum, on loosely packed 50mg. samples, exact comparison of results with T.G.A. cannot be made due to the difference in conditions. However, similar trends should be present and the information obtained should be complementary.

2.8 Gas Chromatography.

Qualitative analysis of the purity of the reactants was carried out, wherever possible, using a Microtek G.C. 2000R Gas Chromatograph with a flame ionisation detector using 1 % silicone gum (S.E. 30) on Embacel 100/120 columns. A linear temperature programme of $10^{o}C$/min., between $50^{o}C$ and $200^{o}C$, was used.

2.9 Elemental Analysis.

Micro-analysis of the polymers was carried out by the complete combustion technique, using a Perkin-Elmer 240 Elemental Analyzer.

2.10 Styrene/Methyl Methacrylate System.

Since only a preliminary investigation into this system was undertaken, it was not thought to be necessary to employ the rigorous, time-consuming procedures described previously, to obtain the high state of purity desired for the styrene system, which was investigated in detail. Instead of working at pressures of less than 10^{-4} torr, all reactions were performed under nitrogen.

a) Purification of Reagents.

Methyl methacrylate (I.C.I. Ltd.) was purified by distillation under vacuum and drying over calcium hydride at $0^{o}C$, as described for styrene. Azobisisobutyronitrile (Eastman Organic Chemicals Ltd.) was recrystallised from ethanol and dried at room temperature for

24 hours in a vacuum oven to ensure complete removal of solvents. The following substituted styrenes,

2,6-dimethyl styrene, m-methyl styrene,
m-chloro styrene, p-methyl styrene,
p-chloro styrene, p-methoxy styrene,

(Koch-Light Laboratories Ltd.) were obtained pure. 95 % ethanol (Burroughs Ltd.) was dried with fresh sodium wire, before use.

All other reagents were purified as described in the previous sections of this chapter and the standard stannic chloride solution was also prepared by the procedure described earlier.

b) Polymer Syntheses.

Values for the reactivity ratios for the free-radical copolymerisation of methyl methacrylate and styrene at 80°C were not listed in the literature. However, the known values of reactivity ratios at different temperatures[89] were plotted against temperature and from the linear relationship obtained, the reactivity ratios for methyl methacrylate (r_A) and styrene (r_B), at 80°C were evaluated as follows,

$$r_A = 0.48$$

$$r_B = 0.54.$$

The ratio of methyl methacrylate to styrene required for the preparation of 1/1, 5/1 and 10/1 copolymers was calculated from the copolymer composition equation, which can be rearranged to give,

$$B^2 r_B dA + AB(dA - dB) - A^2 r_A dB = 0$$

where $\frac{dA}{dB}$ is the ratio of methyl methacrylate to styrene in the desired copolymer,

$\frac{A}{B}$ is the ratio of methyl methacrylate to styrene in the monomer mixture.

During the copolymerisation reaction, the concentrations of the monomers will change as they will react with different velocities. The result of this is that the copolymer composition will change and therefore, no copolymerisation was allowed to proceed beyond 20 % conversion.

A small scale pilot reaction was carried out for each copolymer in a 50 ml. three-necked, round bottom flask. A solution of 2.5 ml. of the calculated monomer mixture and 0.5 g. azobisisobutyronitrile was made up to 25 ml. with ethanol and refluxed under nitrogen, for 30 minutes. On cooling, the copolymer precipitated, was filtered and dried at 80°C in a vacuum oven for 24 hours. It was then reprecipitated from dioxan by pouring into a 50 % methanol/distilled water mixture, filtered and dried as before. The percentage polymerisation was determined by weighing. Knowing the extent of polymerisation obtained in a reaction time of 30 minutes, the copolymerisation time for 20 % conversion was found and used to prepare the series of copolymers on a 500 ml. scale, using similar apparatus. The exact copolymer composition was then determined by elemental analysis, which gave the relative quantities of carbon, hydrogen and oxygen present in each copolymer.

Copolymers of methyl methacrylate with the substituted styrenes and poly(methyl methacrylate) itself were prepared using an identical procedure. Polystyrene was prepared as described earlier and dioxan was removed from all the homopolymers and copolymers by reprecipitation from chloroform, which does not react with stannic chloride.

c) Crosslinking and Cyclisation Reactions.

Quantitative details of these reactions will be given later, as it was found necessary to discuss these with the results obtained. Only the reaction conditions will be given here.

A solution containing known weights of a copolymer, D.C.M.B. and a known volume of standard stannic chloride solution, was made up to 20 ml. with D.C.E. in a 50 ml. round bottom flask, which was then sealed after being flushed with nitrogen. It was immersed in a stirred, thermostatically controlled water bath at 60 ± 0.5°C. This solution was used to investigate the crosslinking reaction, whereas exactly the same solution with no D.C.M.B. present was used to study the cyclisation reaction.

The reaction mixtures were either allowed to gel or were precipitated into a 50 % methanol/distilled water mixture and purified as described previously.

CHAPTER THREE.

PRELIMINARY OBSERVATIONS.

3.1 Introduction.

Before undertaking a detailed kinetic investigation of the reaction between styrene and D.C.M.B., using a Friedel-Crafts catalyst, it was necessary to establish conditions under which the condensation could be conveniently followed. Although only one catalyst is present in the reaction mixture, two distinct condensations are occurring simultaneously. The cationic polymerisation of styrene, which has been studied in detail,[52] is known to be extremely rapid but the Friedel-Crafts alkylation to be used in the crosslinking reaction is much slower.[16] It was, therefore, important to obtain an overall picture of the main features of the two stage process so that the most reliable experimental approach could be determined. As two different reactions are occurring it was also of prime importance to investigate each reactant thoroughly so that possible undesirable side reactions could be either eliminated or avoided.

3.2 Influence of Water.

In many cationic polymerisations catalysed by stannic chloride, water has been shown to act as a cocatalyst[52] and Grassie and Meldrum[16] have also shown that in the reaction between benzene and D.C.M.B., a maximum rate is observed when the $H_2O/SnCl_4$ molar ratio is unity.

For this type of catalysis the mechanism is considered[90] to be,

$$SnCl_4 + H_2O \rightleftharpoons SnCl_4.H_2O$$
$$SnCl_4.H_2O \longrightarrow SnCl_4OH^{\ominus}\ H^{\oplus}$$

At higher concentrations, stannic chloride is precipitated from solution in the form of a hydrate and the accompanying decrease in reaction rate is accounted for by the consequent decrease in stannic chloride concentration in the solution. The decrease in rate at lower water concentrations can be explained by the reduction in the concentration of the $SnCl_4/H_2O$ complex in favour of the less active stannic chloride catalyst.

However, although water is a cocatalyst, reaction was still found to occur at zero water concentration and this is supported by Colclough and Dainton's[91] observation that the cationic polymerisation of styrene by stannic chloride in D.C.E. occurs in the absence of water.

The presence of water, therefore, greatly affects the rate of Friedel-Crafts reactions of the types under investigation and in order to obtain reproducible results the concentration of water must be accurately controlled. To achieve easy reproducibility, the most convenient method of controlling the water concentration was to eliminate it completely by the rigorous drying procedures described in Chapter 2 and to carry out all rate measurements under vacuum. These procedures minimise contamination and good reproducibility was obtained throughout the study.

3.3 Influence of D.C.E.

If the solvent itself can act as a cocatalyst, drying will never reduce the condensation reaction rate to zero. Pepper[48] has shown that D.C.E. exhibits cocatalytic properties in reactions of the type under investigation, but it is only a cocatalyst in polar media, such as itself when used as the solvent. This is due to the higher solvation energy of a polar medium,[50,51] which enables solvation stabilisation of the ion-pair. D.C.E., however, is not a cocatalyst when present as a reactant in a non-polar medium. The mechanism suggested by Pepper[48] for the cocatalytic activity of D.C.E. towards stannic chloride may be represented as,

$$SnCl_4 + (CH_2Cl)_2 \longrightarrow SnCl_5^{\ominus} + ClC_2H_4^{\oplus}$$

Thus, the reactions under discussion are accelerated by using D.C.E. as solvent.

3.4 Influence of HCl.

HCl is a useful product of the styrene/D.C.M.B. condensation since it can be used to follow the progress of the reaction. However, it has been shown[48] that HCl itself is a catalyst for Friedel-Crafts reactions in polar media, irrespective of the presence of water and also that in the presence of stannic chloride,[51] HCl can act as a cocatalyst, by the following mechanism,

$$SnCl_4 + HCl \longrightarrow SnCl_5^{\ominus} \quad H^{\oplus}$$

As in the case of the solvent, the HCl produced accelerates the reaction in polar media. This is another example of solvation stabilisation of the ion-pair in polar media.

3.5 Self-Condensation of D.C.M.B.

It was important to establish whether D.C.M.B. would undergo significant self-condensation under the reaction conditions employed, since this would make branching possible and thus a correction would be required when calculating the degree of crosslinking. Mixtures of various concentrations of D.C.M.B. and stannic chloride in D.C.E. were allowed to react at 30°C and the quantity of HCl produced was estimated by titration with standard alkali. No reaction could be detected after long periods and so it was assumed that the rate of self-condensation of D.C.M.B. is negligible compared with the rate of condensation of styrene with D.C.M.B.

3.6 Cationic Polymerisation of Styrene.

If the crosslinking reaction is to be followed by molecular weight measurements, then it is essential that the polystyrene formed in the styrene/$SnCl_4$/D.C.M.B. mixture should have a molecular weight which is independent of reaction conditions.

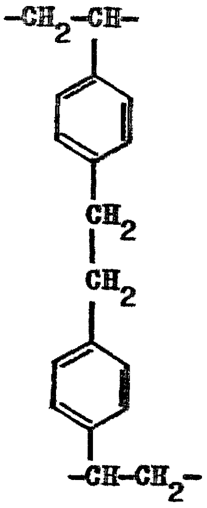
Although not very much work has been done on molecular weight distribution of polystyrene produced cationically, Pepper and Burton[36] have shown that polymers isolated at very low conversions should have the 'most probable' distribution as found in condensation polymerisations and that as the reaction proceeds the distribution should broaden, shifting its maximum to a lower chain length. This has been confirmed experimentally by Albert and Pepper.[38] In order to test this in the present reactions, solutions of identical concentrations of styrene and stannic chloride in D.C.E. were polymerised for varying times and purified by the methods outlined in Chapter 2. It was found that the $\overline{M}_n$ decreased from 12,000 after 30 minutes reaction time to 9,000 after 300 minutes reaction time, which confirmed the above predictions.

Identical solutions of styrene and stannic chloride in D.C.E. were also polymerised for 300 minutes in the presence of varying known quantities of D.C.M.B. and it was found that as the D.C.M.B. concentration increased, the $\overline{M}_n$ decreased from 12,000 with no D.C.M.B. present to 7,000 with a high concentration of D.C.M.B. This may be due to termination of the polymerising styrene by hydrochlorination.[92,93] Also Colclough and Dainton[50,51] have shown that the degree of polymerisation of styrene catalysed by stannic chloride in D.C.E. is proportional to the styrene concentration but independent of the stannic chloride concentration.

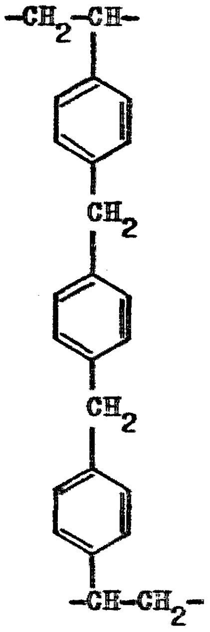
It appears, therefore, that the initial molecular weight of the polystyrene formed in the condensation between styrene and D.C.M.B. is dependent upon reaction time, D.C.M.B. concentration and styrene concentration. The molecular weight of the polystyrene will differ for each combination of reactants required for a complete kinetic investigation. Any results derived from $\overline{M}_n$ measurements must, therefore, be cautiously investigated and examined.

3.7 Miscellaneous Competing Reactions.

Bevington and Norrish[72] reported that polystyrene can be crosslinked by D.C.E. using aluminium trichloride as the catalyst giving crosslinks with structure (a), which is similar to the desired crosslink structure (b). As HCl is also evolved as a reaction product, there is no obvious method of distinguishing between the two types of crosslinks. It is, therefore, important to determine the extent of the former crosslinking process under the reaction conditions to be used.



(a)



(b)

Experiments were performed by reacting mixtures of various concentrations of styrene and stannic chloride in D.C.E. for varying times and the degree of reaction estimated by titration with standard alkali. It was found that under the wide range of concentrations used, no crosslinking reaction could be detected and so it was concluded that the only two reactions which do occur under the conditions selected for this study are the desired cationic polymerisation of styrene and the Friedel-Crafts alkylation between styrene and D.C.M.B.

3.8 Styrene/D.C.M.B. Condensation.

a) Introduction.

The influence of each reactant having been determined, it was

Table 1.

Concentrations of Reactants in the Styrene/D.C.M.B. Condensations.

Series	(D.C.M.B.) (mole/l.)	(Styrene) (mole/l.)	($SnCl_4$) (mole/l.)
4	0.338	0.875	0.00451
5	0.676	0.875	0.00451
6	1.352	0.875	0.00451
7	1.014	0.875	0.00451

now possible to proceed with some preliminary experiments which demonstrate the feasibility of using Friedel-Crafts condensations to produce crosslinked polystyrene in a two stage process consisting of prepolymerisation, followed by curing. Since both the polymerisation of styrene and the condensation of D.C.M.B. with aromatic nuclei can be initiated by Friedel-Crafts catalysts, it should be possible to produce crosslinked polystyrene in a one step process by mixing styrene, D.C.M.B. and stannic chloride in the appropriate proportions.

10 ml. reaction vessels were filled with known quantities of styrene, D.C.M.B., stannic chloride and D.C.E. by the procedures described in Chapter 2 and the reactions were considered to start from the time thawing commenced. The reactions were carried out at 30°C and were terminated using the methods detailed in Chapter 2. Initially, all reaction mixtures were clear and colourless but as the reaction proceeded a yellow colour developed. This gradually deepened, through orange, to the deep red colouration which was present at the onset of gelation. Also, the solutions became more viscous as the reactions proceeded but at no time did they loose their transparency. Addition

of water to the reaction mixture or precipitation into methanol resulted in rapid discharge of the deep red colouration in favour of a colourless solution and a fine white precipitate, which was purified by the techniques described in Chapter 2. The concentrations of reactants used for all the reactions investigated are presented in Table 1.

b) Estimation of the Degree of Crosslinking from HCl Evolution.

Using the procedure described in Chapter 2, the quantity of HCl evolved during each reaction was determined by titration with standard alkali and the results are tabulated in Table 2. Typical plots of volume of 0.1N NaOH required for neutralisation versus reaction time for certain series of reactant concentrations are presented in Figure 20. The intercept is associated with neutralisation of the stannic chloride present in the reaction mixture and so this amount must be subtracted from each titre to obtain the true volume of alkali required to neutralise the HCl evolved during the formation of crosslinks. Typical plots of HCl evolved versus reaction time are shown in Figure 21. The linearity of the plots demonstrates that the rate of HCl evolution is constant.

c) Estimation of the Degree of Crosslinking from Ultra-violet Spectroscopy.

Linear polystyrene and polystyrenes with varying degrees of crosslinking were synthesised and purified using the procedures detailed in Chapter 2. Ultra-violet spectra of polystyrene and two crosslinked polystyrenes are shown in Figure 22. Crosslinking is clearly associated with the absorption shoulder at 276mμ. Figure 23 shows ultra-violet spectra of o,m and p xylenes, which have absorption maxima at 272, 274 and 276mμ, respectively. p-Dibenzyl benzene gives an identical spectrum to that of p-xylene.

Assuming that the shoulder at 276mμ in the crosslinked polystyrene

Table 2.

Relationship between HCl Evolution and Reaction Time.

Series	Reaction Time (hours)	(HCl) Evolved (mole/l.) Titration	(HCl) Evolved (mole/l.) Ultra-violet
4	5	0.0046	0.0066
4	42	0.0356	-
4	54	-	0.040
4	72	0.0619	0.060
4	78	-	0.066
5	5	0.0092	0.006
5	24	0.035	-
5	29	-	0.034
5	42	0.060	-
5	53	-	0.060
5	75	-	0.100
6	5	0.0092	0.0066
6	48	0.092	0.100
6	72	0.133	0.133
7	5	0.0092	0.0134
7	42	0.0745	-
7	54	-	0.0934
7	72	0.128	0.120

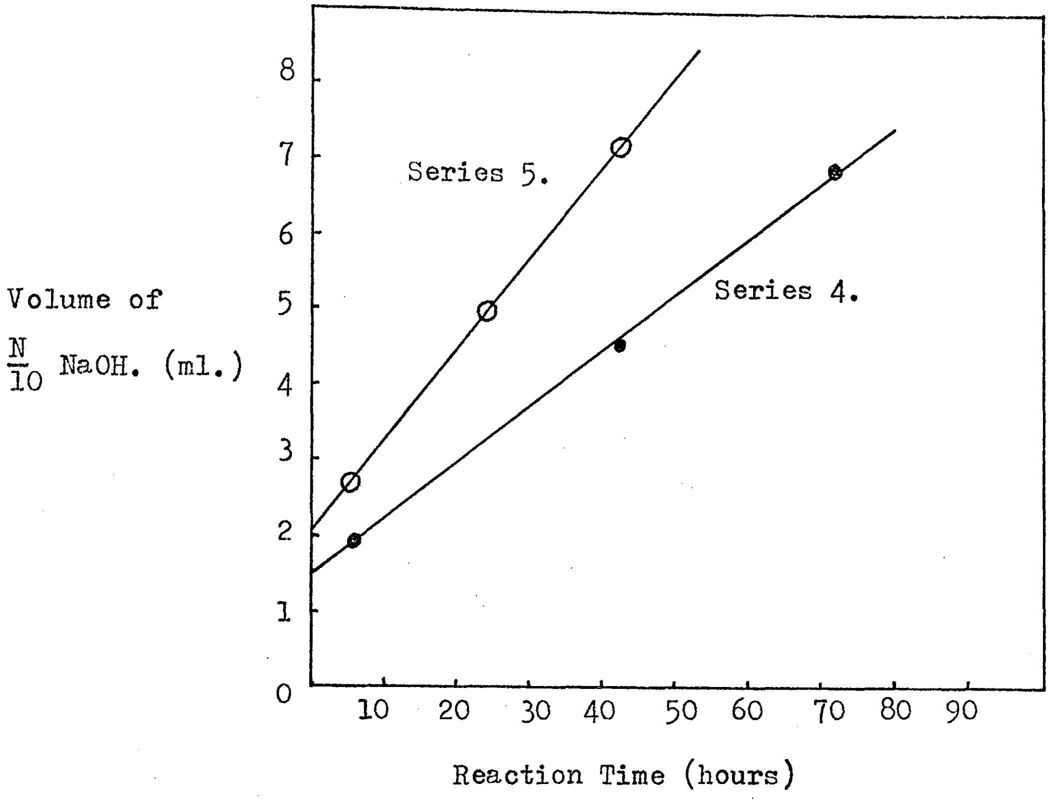


Figure 20. Relationship between Titre and Reaction Time.

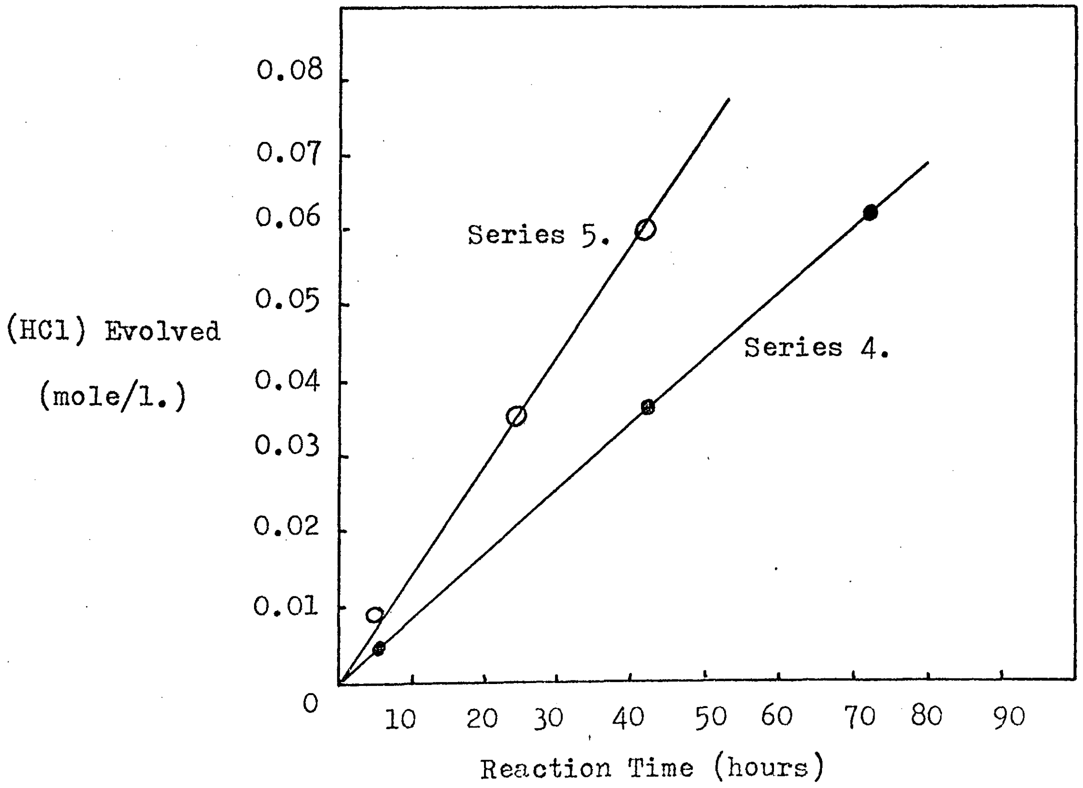


Figure 21. Relationship between (HCl) Evolved and Reaction Time.

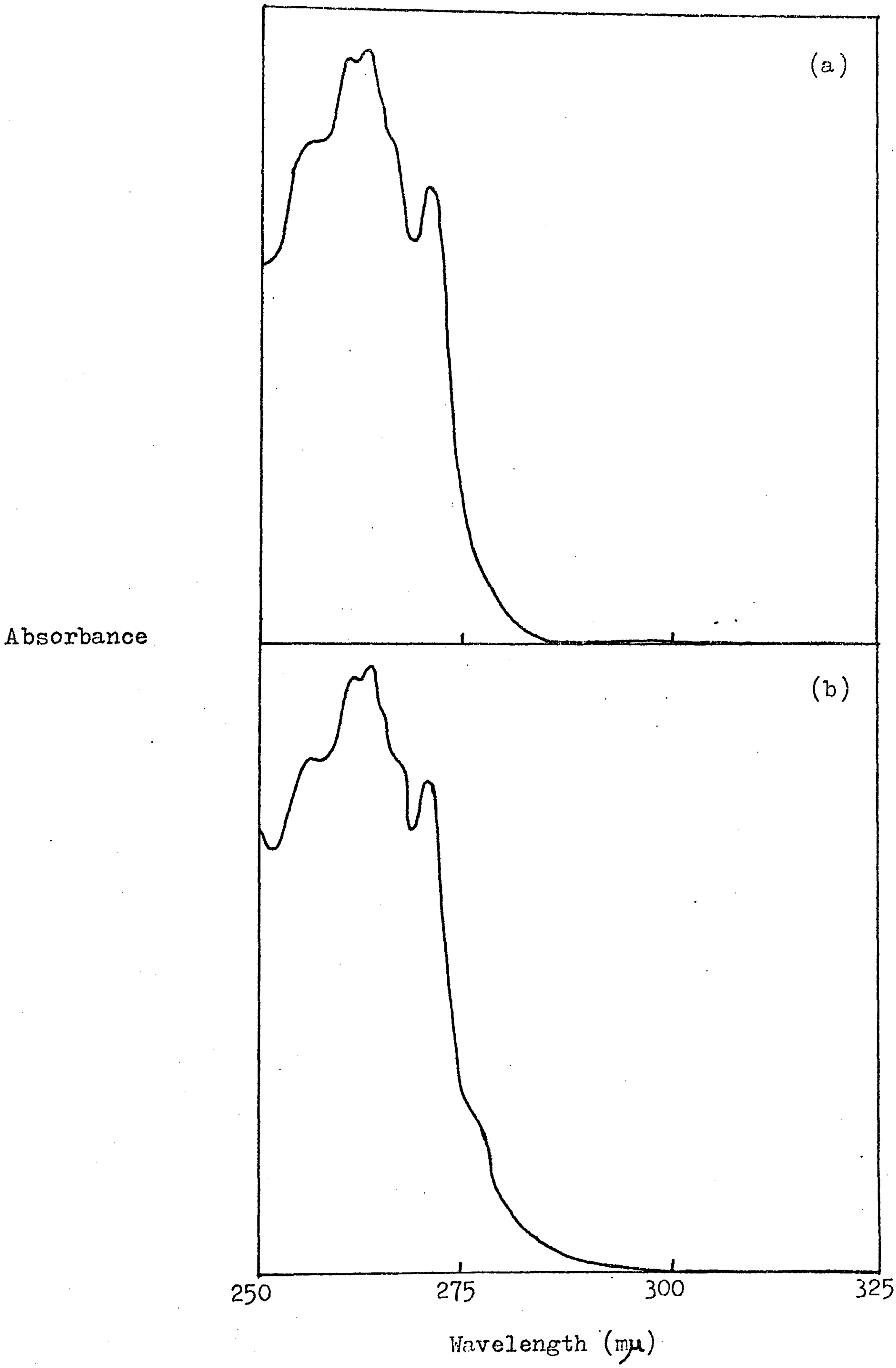
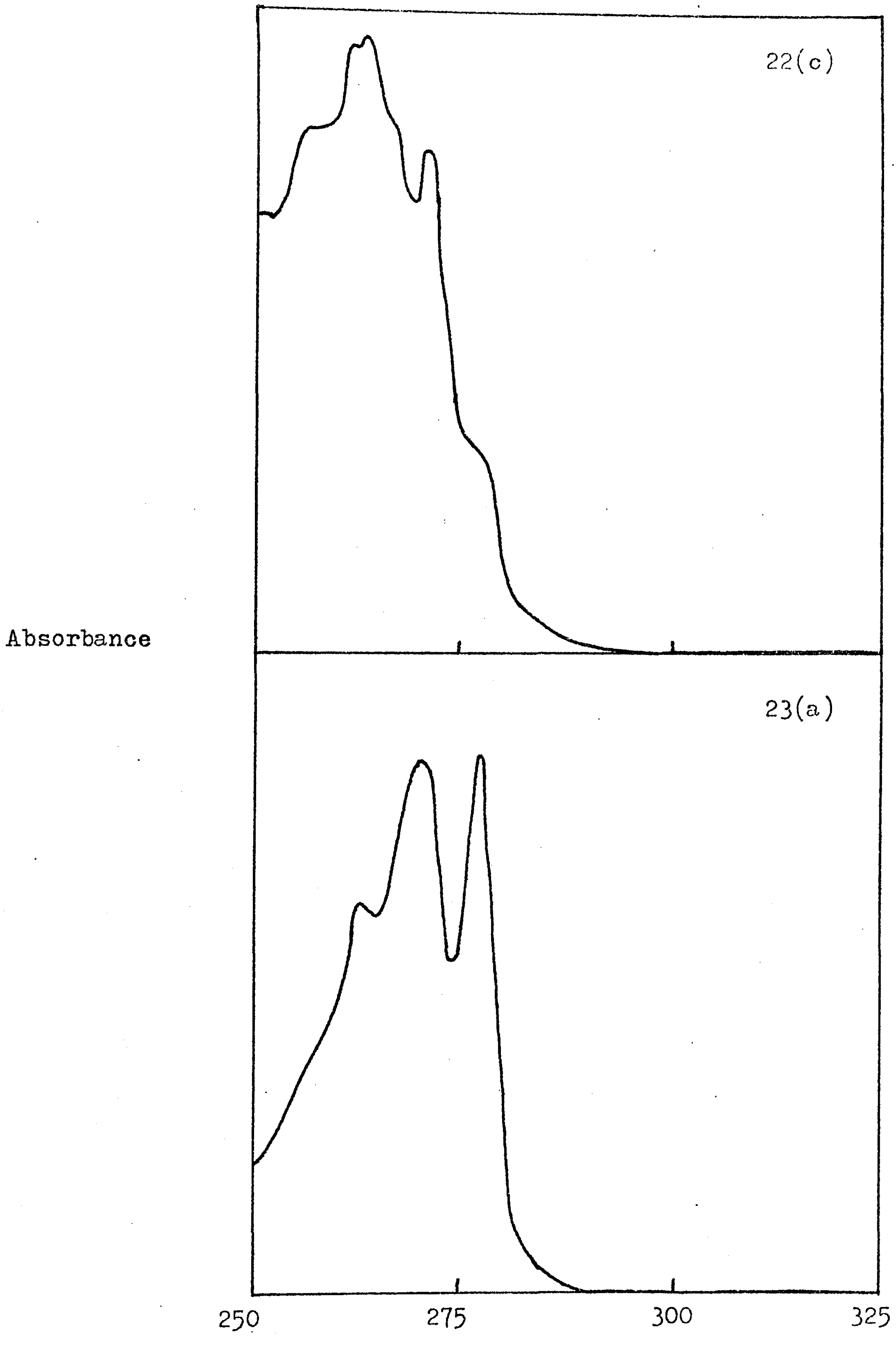


Figure 22. Ultra-violet Spectra of (a) Polystyrene and (b) Polystyrene Crosslinked for 54 hours (Series 4.).



Figures 22 and 23. Ultra-violet Spectra of 22(c) Polystyrene Crosslinked for 78 hours (Series 4.) and 23(a) p-xylene.

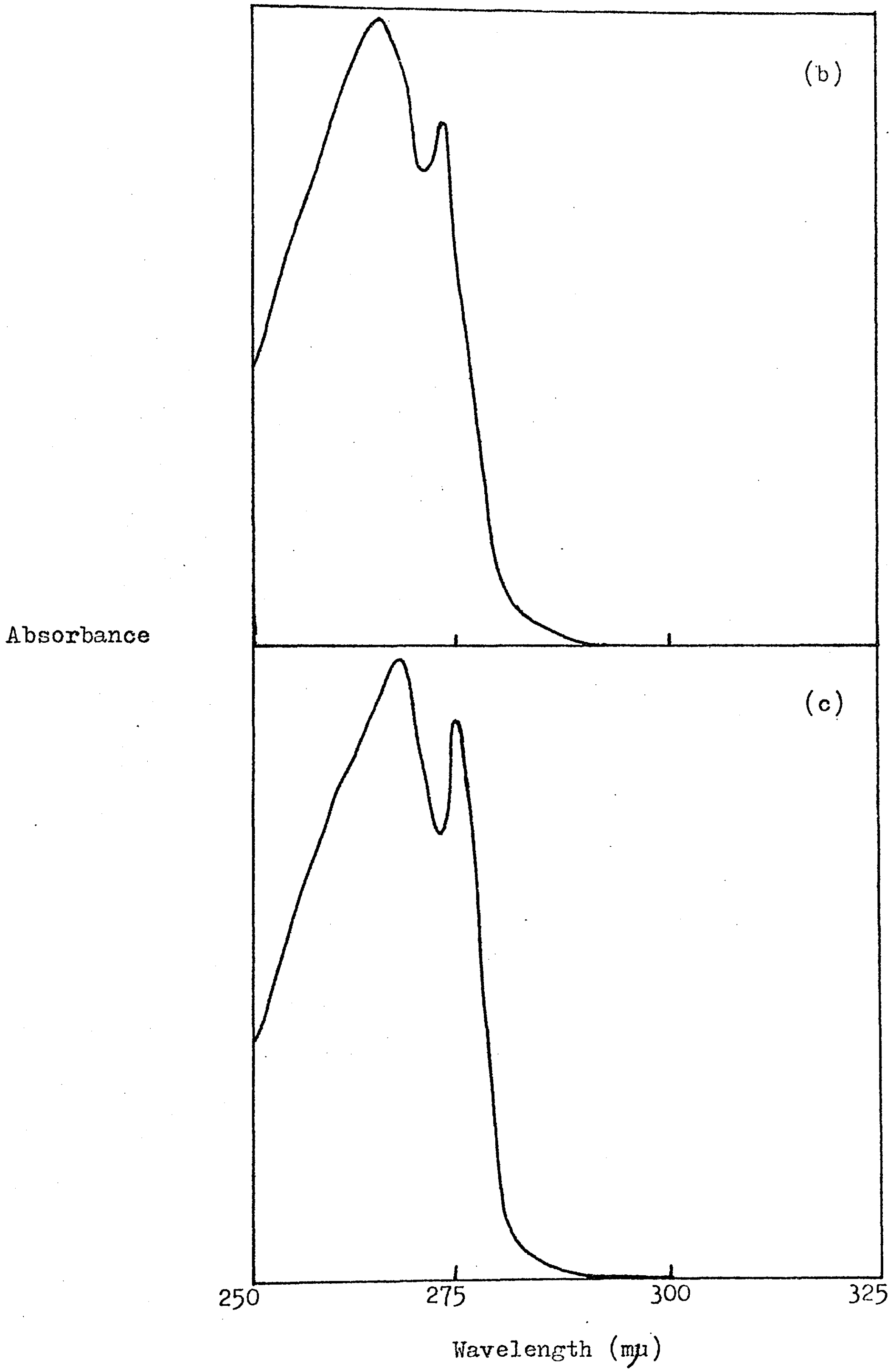


Figure 23. Ultra-violet Spectra of (b) o-xylene and (c) m-xylene.

samples is due to para disubstituted benzene rings, this suggests that one crosslink consists of the predicted structure of three para disubstituted benzene rings, as shown in Chapter 3.7(b), due to the directing properties of substituted benzene rings.

From quantitive ultra-violet spectra, similar to those shown in Figures 22 and 23, the molar absorbances of polystyrene, all the crosslinked polystyrenes and p-xylene, at 276mμ, were calculated[94] using the expression,

$$\text{Absorbance} = \log.\frac{I_0}{I} = \epsilon.l.c$$

where I_0 = incident beam intensity,

I = transmitted beam intensity,

ϵ = molar absorbance,

l = path length (cm.),

c = concentration (mole/l.).

The concentration term was calculated in terms of the molecular weight of the styrene monomer unit. The molar absorbances of the polymers were found to increase linearly with reaction time and typical examples are plotted in Figure 24.

If the value of the intercept is again subtracted from the value of the molar absorbance at each reaction time, then the molar absorbances due solely to the crosslinks may be determined and the absolute number of crosslinks may be calculated as follows.

The absorbance of 1 mole of p-xylene = 500.

Let the molar absorbance of the crosslink units in a certain sample = x.

Then, in that polymer sample,

Number of moles of p-xylene $= \dfrac{x}{500}$

Number of moles of crosslinks $= \dfrac{x}{500.3}$

Number of moles of HCl evolved $= \dfrac{2x}{1500}$

Using this expression, the concentration of HCl evolved during a certain reaction time was calculated from ultra-violet data and typical examples of HCl evolution versus reaction time are shown in Figure 25, the values being presented in Table 2. It can be seen that since the concentration of HCl evolved increases linearly with reaction time, a constant rate of HCl evolution was obtained.

It has, therefore, been demonstrated that two methods are available for the determination of HCl evolution and thus the number of crosslinks present in a particular sample, since two HCl molecules are liberated after the formation of one crosslink. Figures 26 and 27 show typical examples of the results obtained by the two procedures, for HCl evolution versus reaction time, superimposed on one graph. The results are collected in Table 2. It can be seen that, within the limits of experimental error, the results are identical, a linear relationship of identical gradient being obtained by the two methods.

The results obtained by the ultra-violet spectroscopy method were calculated using p-xylene as a standard and since the results are in excellent agreement with those obtained from direct titration of the HCl evolved, this is evidence for the Friedel-Crafts alkylation occurring at the para position in the styrene nucleus. This is where substitution is expected due to the ortho and para directing influence of the polystyrene alkyl backbone and to the steric hindrance at the

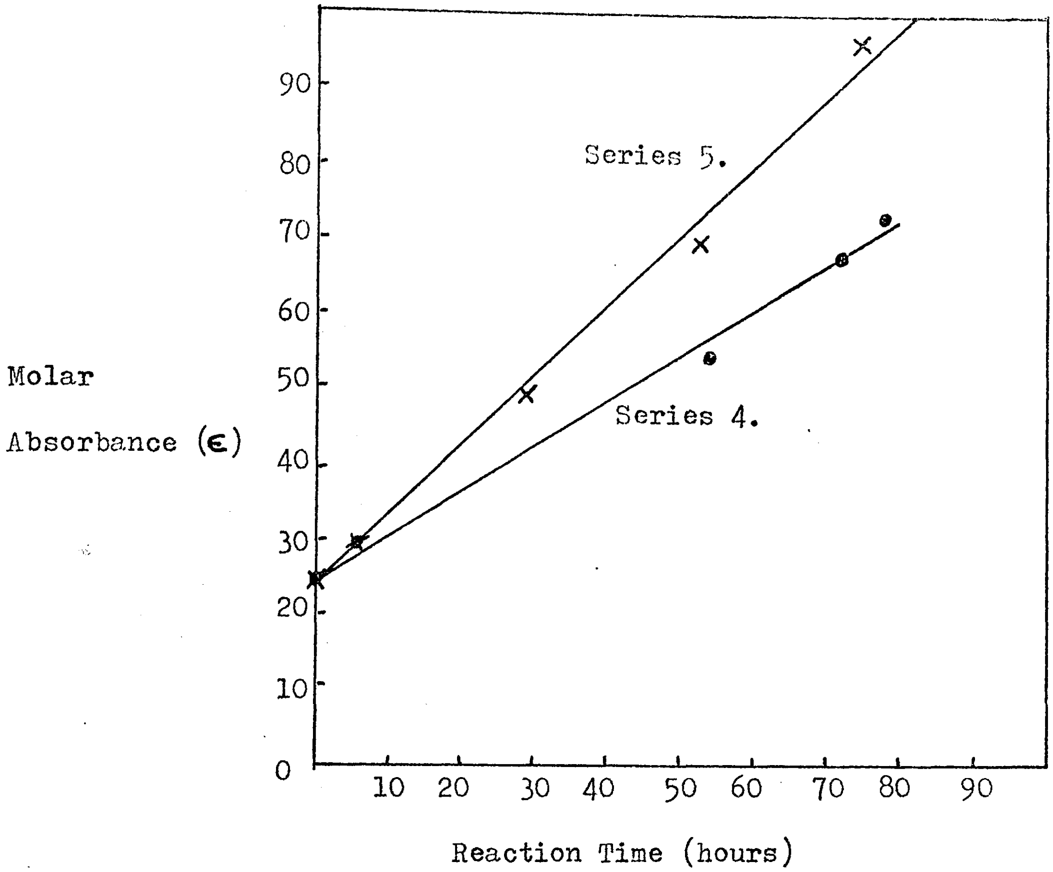


Figure 24. Relationship between Molar Absorbance and Reaction Time.

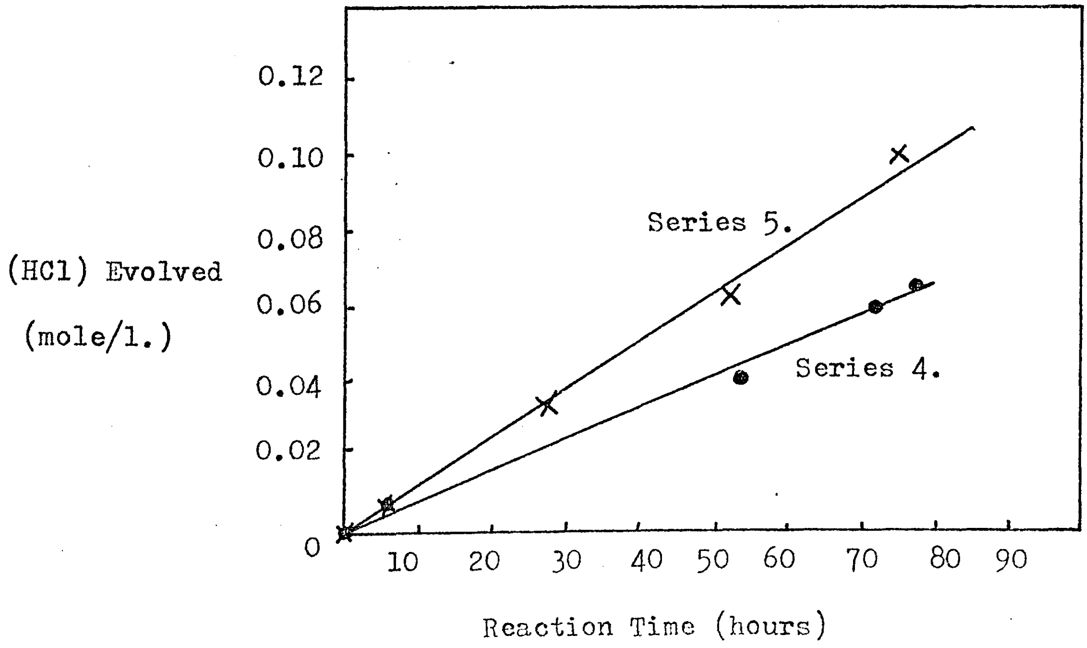


Figure 25. Relationship between (HCl) Evolved and Reaction Time.

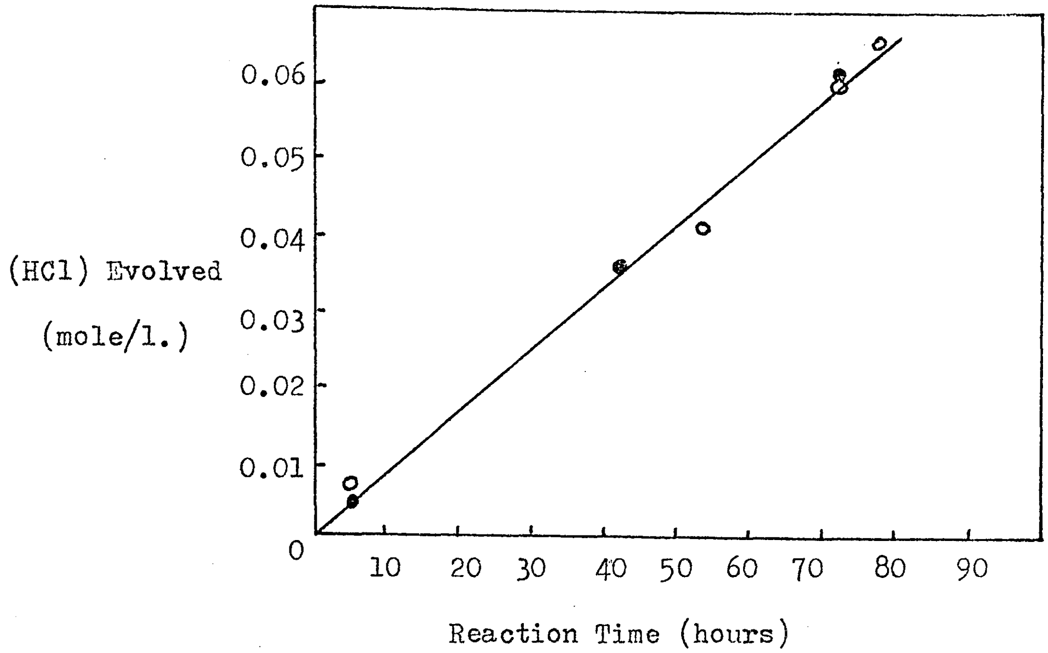


Figure 26. Comparison between (HCl) Evolved, Calculated from (●) Titres and (○) U.V. Spectroscopy. (Series 4.)

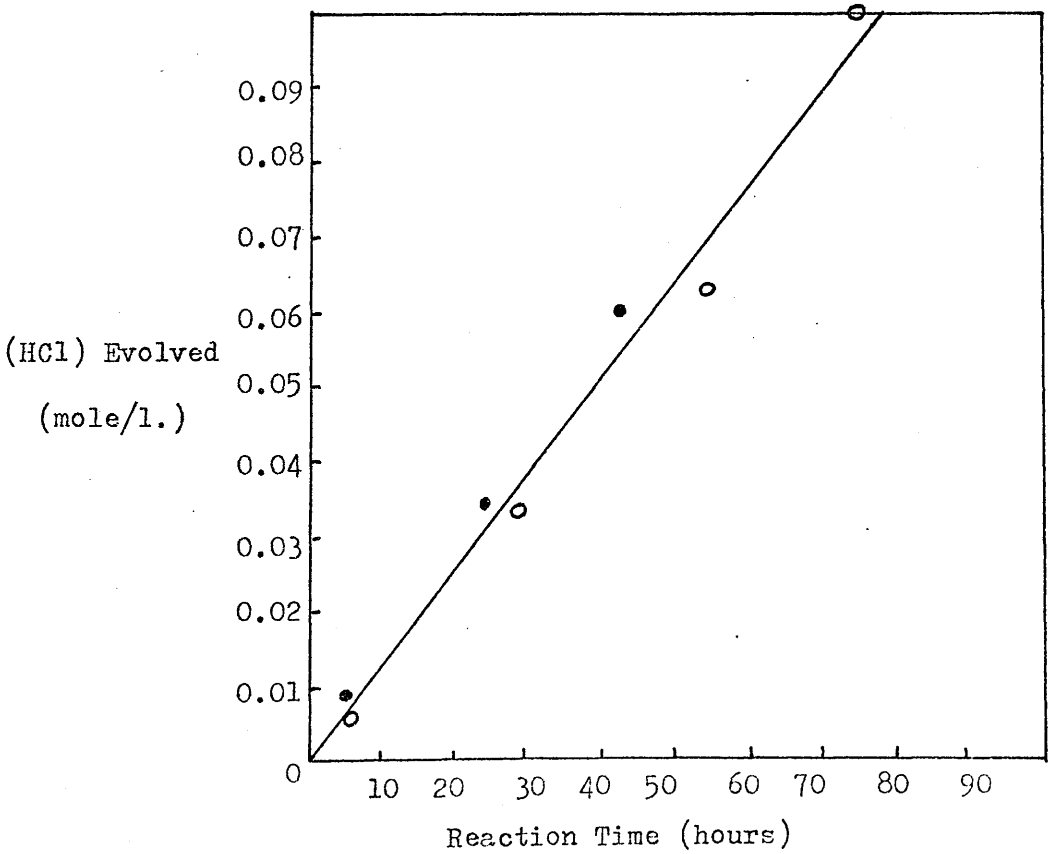


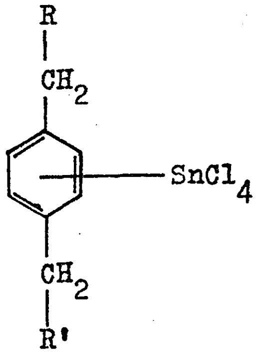
Figure 27. Comparison between (HCl) Evolved, Calculated from (●) Titres and (○) U.V. Spectroscopy. (Series 5.)

ortho and meta positions.

d) Investigation into the Colouration Effect.

As the crosslinking reaction proceeds the colour of the solution darkens as stated previously. Stannic chloride is known[52] to form acceptor complexes with many donor molecules and so the following tests were performed to determine the source of the colouration.

Polystyrene, polystyrene with D.C.M.B., D.C.M.B., crosslinked polystyrene and crosslinked polystyrene with D.C.M.B. were all dissolved in a solution of stannic chloride in D.C.E. Only the solutions containing crosslinked polystyrene became coloured showing that an activated disubstituted benzene ring is required for complex formation. No colouration occurs with D.C.M.B. presumably because the disubstituted benzene nucleus is deactivated by the chloromethyl groups. Also, solutions of p-xylene with stannic chloride and p-dibenzyl benzene with stannic chloride in D.C.E. give red colourations and so under these conditions, the complex must be of the form,



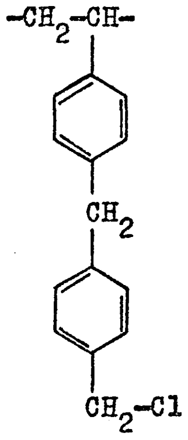
where R and R' are activating substituents.

It was considered outwith the scope of this thesis to undertake a quantitative investigation of this complex formation mechanism.

e) Infra-red Analysis.

No differences could be detected between the spectra of the parent polystyrene and the crosslinked polystyrene samples. A typical spectrum is shown in Figure 28.

Two points arise from the results of the infra-red spectroscopy. The first is that there was no absorption in the region of 850 $cm.^{-1}$ due to disubstituted benzene rings. Secondly, no absorption was observed in the region of 675 $cm.^{-1}$ due to pendant chloromethyl groups, which would be present as a result of partial reaction of D.C.M.B.



Disubstituted benzene rings, however, were detected by ultra-violet spectroscopy and so it was concluded that infra-red spectroscopy is not sensitive enough for these investigations, due to the low concentrations of crosslinks present.

f) N.M.R. Analysis.

As in the case of infra-red spectroscopy, the spectra of polystyrene and all the crosslinked polystyrenes were identical. A typical N.M.R. spectrum is shown in Figure 29. There are no resonances at 7.8 τ and 5.5 τ due to a disubstituted benzene ring or a pendant chloromethyl group, respectively.

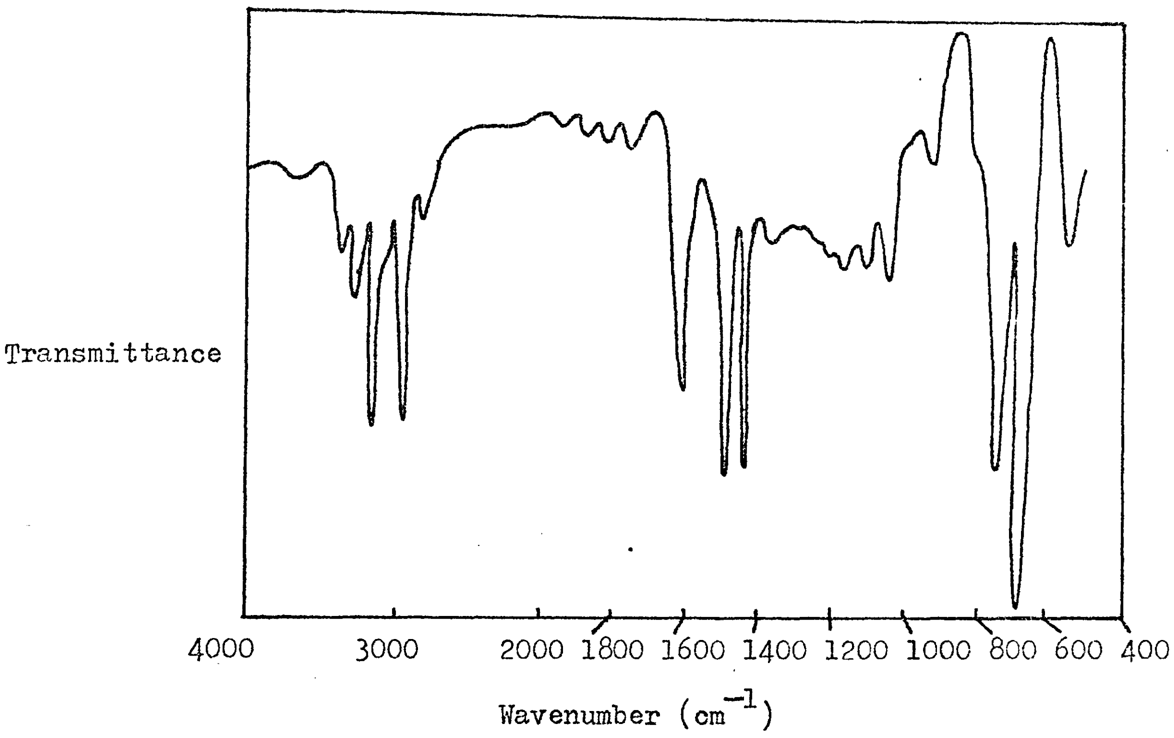


Figure 28. Infra-red Spectrum of Polystyrene.

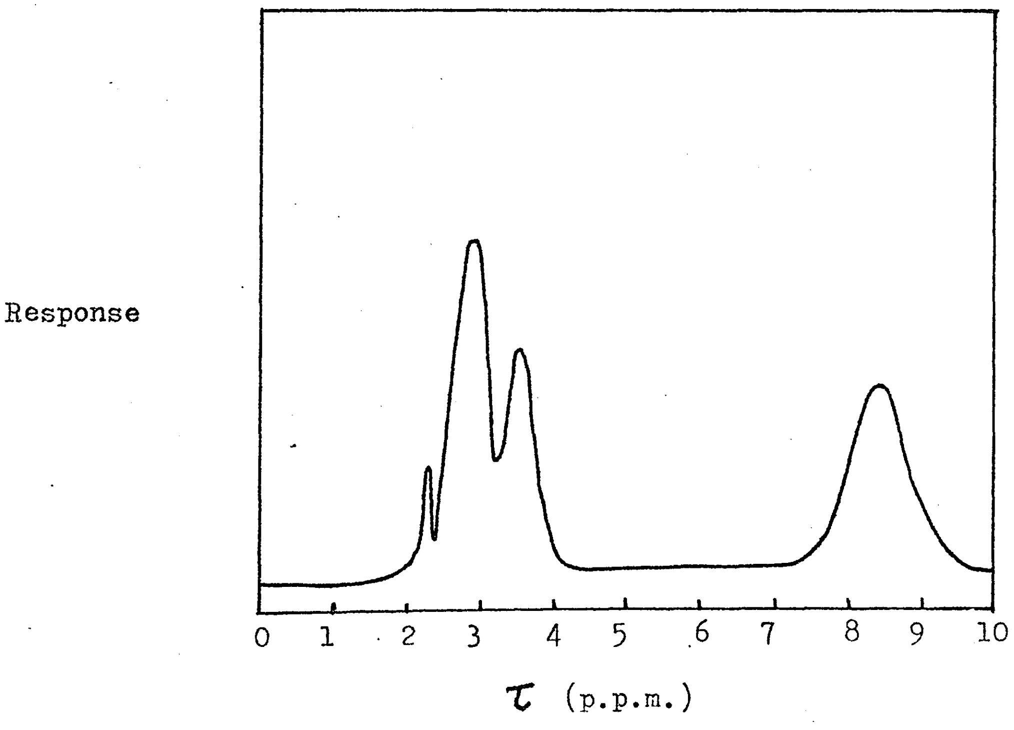


Figure 29. N.M.R. Spectrum of Polystyrene.

It was hoped that either infra-red spectroscopy or N.M.R. spectroscopy would indicate whether pendant chloromethyl groups exist but since crosslinks cannot be detected by these techniques, it cannot be assumed that pendant chloromethyl groups do not exist simply because no evidence of their presence can be found. The second chloromethyl group is much more reactive in the benzene/D.C.M.B.[16] and thiophene/D.C.M.B.[24] systems and so in the polystyrene/D.C.M.B system no chloromethyl groups should exist but this higher reactivity may be influenced by steric effects which do not exist in these other cases.

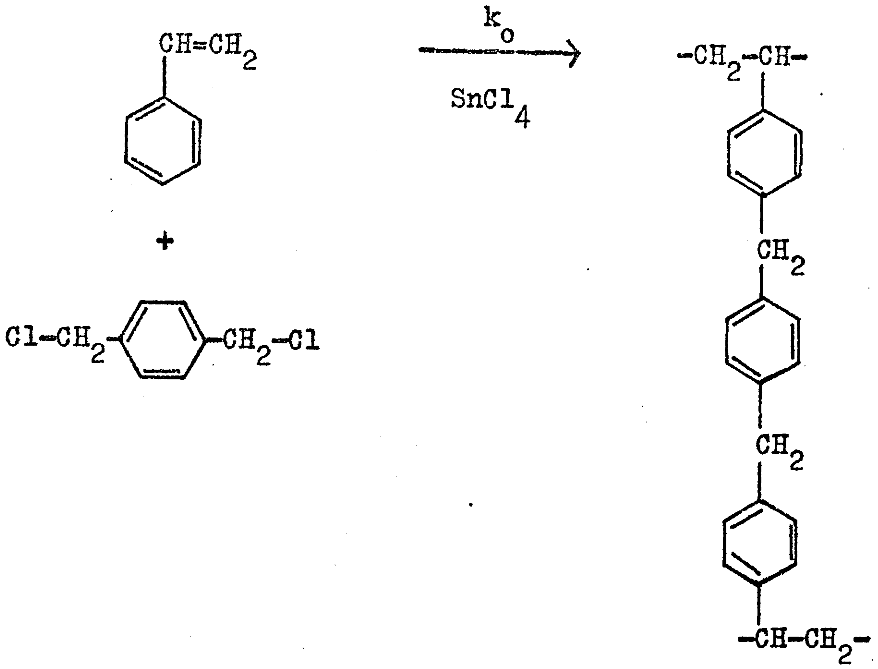
g) Elemental Analysis.

Since the crosslinked polystyrenes and linear polystyrene consist of only carbon and hydrogen, no information about the structure of the crosslinks could be made using elemental analysis. However, the presence of chlorine in a sample can be detected qualitatively, even in extremely small percentages. No evidence for chlorine was found, irrespective of the degree of crosslinking and so it was deduced that there are no pendant unreacted chloromethyl groups present in the crosslinked polymers.

h) Kinetic Investigations.

Having obtained linear plots for HCl evolution versus reaction time, for each series of concentrations of reactants, the gradients of the lines, which denote the rate of evolution of HCl were plotted versus the initial D.C.M.B. concentration to obtain the smooth curve shown in Figure 30.

The overall reaction between styrene and D.C.M.B. consists of many steps which will be discussed in detail at a later stage but at this point only the overall reaction need be considered.



The following rate equation describes this reaction,

$$\text{Rate} = k_o(\text{D.C.M.B.})^x(\text{Styrene})^y(\text{SnCl}_4)^z$$

where x,y and z are the orders of the reaction with respect to D.C.M.B., styrene and stannic chloride, respectively. Since only the concentration of D.C.M.B. has been varied at this stage, the above equation may be simplified to give,

$$\text{Rate} = k_1(\text{D.C.M.B.})^x$$

where $k_1 = k_o(\text{Styrene})^y(\text{SnCl}_4)^z$.

This equation may now be written in the form,[95]

$$\log.(\text{Rate}) = \log.k_1 + x\log.(\text{D.C.M.B.})$$

If log.(Rate) is plotted against log.(D.C.M.B.), the gradient of the

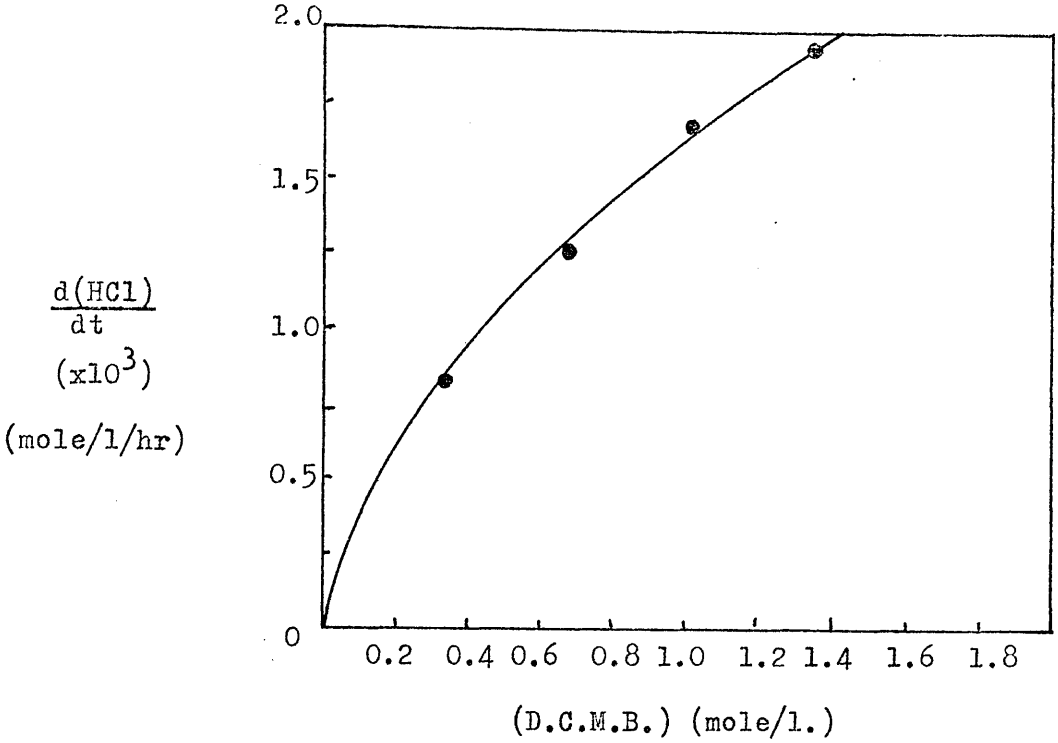


Figure 30. Relationship between Rate of HCl Evolution and (D.C.M.B.)

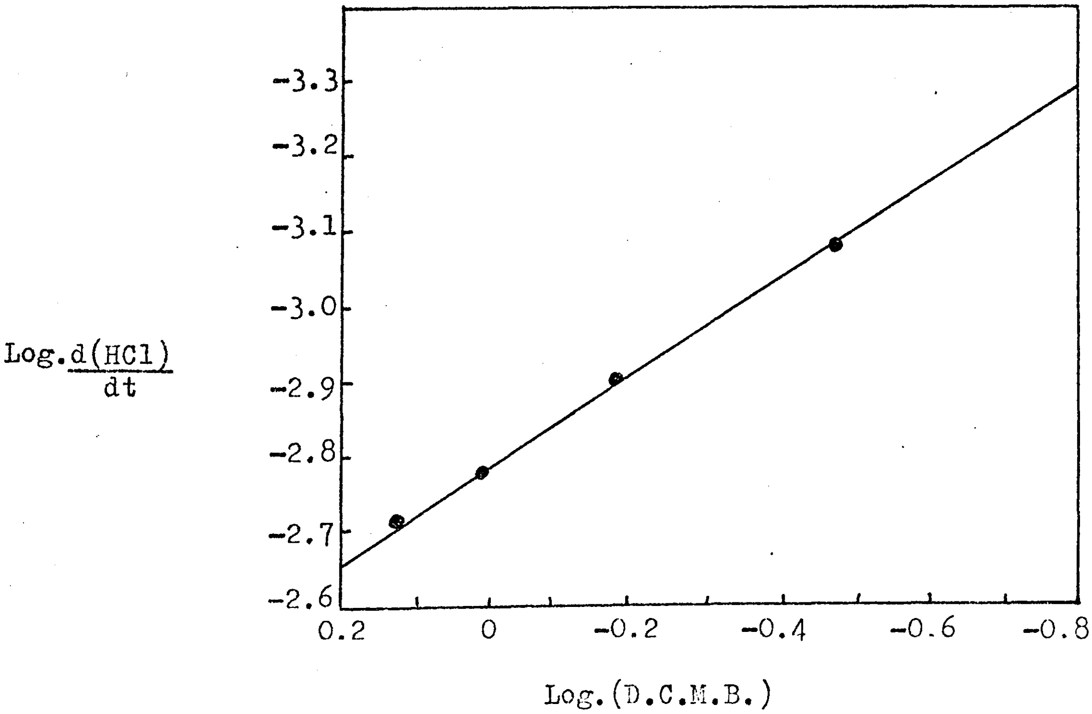


Figure 31. Logarithmic Relationship between Rate of HCl Evolution and D.C.M.B. Concentration.

Table 3.

Dependence of Rate of HCl Evolution upon D.C.M.B. Concentration.

Series	(D.C.M.B.) (mole/l.)	log.(D.C.M.B.)	$\frac{d(HCl)}{dt}$ ($\times 10^3$) (mole/l/hr)	log.$\frac{d(HCl)}{dt}$
4	0.338	-0.471	0.834	-3.078
5	0.676	-0.170	1.26	-2.90
6	1.352	0.131	1.94	-2.712
7	1.014	0.006	1.68	-2.775

straight line obtained represents the order of the reaction with respect to the D.C.M.B. concentration. This is shown in Figure 31 and the results are presented in Table 3. Using this method, an order of 0.65 with respect to the D.C.M.B. concentration was obtained.

$$\text{Rate} = k_1(\text{D.C.M.B.})^{0.65}$$

3.9 Conclusions.

These preliminary experiments have demonstrated that crosslinked polymers can be produced by the method described in this chapter. However, although both the polymerisation of styrene and the condensation of the aromatic nuclei with D.C.M.B. are initiated by Friedel-Crafts catalysts, it became clear that it is impossible, by simple manipulation of variables such as temperature and concentration of reagents, to find a set of conditions under which the reactions will proceed at comparable rates to give the desired products. The polymerisation of styrene is so much faster than the crosslinking condensation that it is virtually complete before a significant amount of the crosslinking reaction has occurred. Since it has been shown in Chapter 2 that approximately 40 % conversion of styrene to polystyrene had occurred after 30 minutes reaction time and Figures 26 and 27 show that for the crosslinking reaction, reaction times of up to 80 hours are being studied, it may be estimated that the cationic polymerisation of styrene is in the order of 150 times faster than the condensation between aromatic nuclei and D.C.M.B.

The true concentration of the initiator participating in the crosslinking process may be influenced by the polymerisation phase and so it would be much more satisfactory to start from polystyrene in any mechanistic and kinetic investigation of crosslinking. Also, it has been shown that the molecular weight of the initial polystyrene varies with reaction time, D.C.M.B. concentration and styrene concentration and so more satisfactory results should be obtained using preformed linear polystyrene. Low molecular weight polystyrene should be used so that gelation will occur less quickly.

CHAPTER FOUR.

CROSSLINKING OF POLYSTYRENE.

4.1 Introduction.

The preliminary investigations in Chapter 3 have shown that as the cationic polymerisation of styrene is much faster than the condensation between the aromatic nuclei and D.C.M.B., the two processes are consecutive rather than concurrent, when one starts with a mixture of monomeric styrene, D.C.M.B. and stannic chloride. Since the percentage conversion and thus the time of polymerisation of styrene is known to affect its molecular weight distribution,[36,38] a quantitative study of the condensation process should be facilitated by starting with the polymer rather than the monomer. This chapter, therefore, is concerned with the kinetics of the reaction between D.C.M.B. and the aromatic nuclei in the preformed polystyrene. The polystyrene used in the reaction will, therefore, have a constant, known molecular weight which does not vary with reaction time or reactant concentrations and also the concentration of the stannic chloride present will not be upset by the prepolymerisation step.

4.2 Synthesis of Polystyrene.

Cationic polystyrene was prepared and purified using the procedures described in detail in Chapter 2. A large enough quantity was prepared initially in order to ensure that the whole investigation involved identical material. The number average molecular weight of the purified polystyrene, measured by membrane osmometry as described in Chapter 2, was 13,500. As the purpose of these experiments was to determine the variation in the degree of crosslinking with reaction time, it was desirable to commence with low molecular weight polystyrene so that the greatest possible extent of reaction could be achieved before the onset of insolubility or gelation.

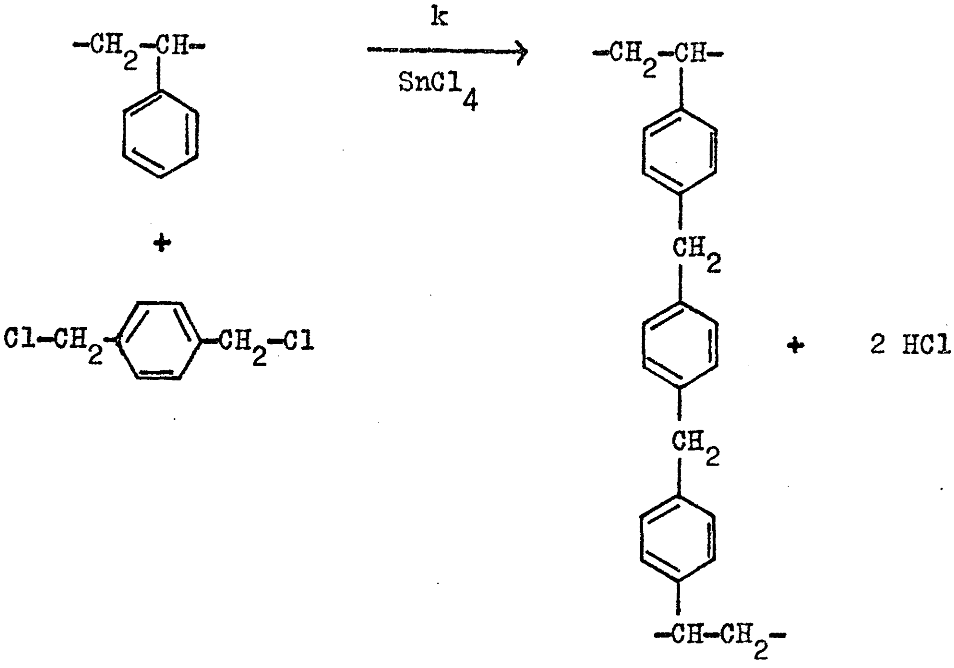
Using the spectroscopic techniques described in Chapter 2, the purity of the polystyrene was checked. Ultra-violet, infra-red and N.M.R.[96] spectra are shown in Figures 22(a), 28 and 29, respectively. In all cases, the spectra showed that the polystyrene was extremely pure and in no spectra were solvent residues detected. Also, no trapped solvent was detected when the polystyrene was heated above its glass transition temperature using Thermal Volatilisation Analysis.[88]

4.3 Polystyrene/D.C.M.B. Condensation.

a) Identification of Products.

After mixtures of various known concentrations of polystyrene, D.C.M.B. and stannic chloride in D.C.E. had been allowed to react for known times at 30°C, the reactions were terminated and the products purified by the methods detailed in Chapter 2. If the overall reaction is as shown overleaf, then close examination of the system shows that both intermolecular and intramolecular crosslinks may be formed. It is, therefore, necessary to determine the relative amounts of each type of crosslink and to determine the kinetics for each reaction. The concentrations of reactants used in these kinetic investigations are presented in Table 4.

As the possibility of the existence of pendant chloromethyl groups in the crosslinked polymers has now been eliminated, it follows that all the disubstituted aromatic nuclei detected by ultra-violet spectroscopy must be due to crosslinks.



It has also been shown that under the reaction conditions chosen for these experiments, crosslinking by D.C.E. does not occur and so all the crosslinks must consist of the above structure, incorporating three para disubstituted aromatic nuclei.

b) Determination of the Degree of Crosslinking.

The procedure for the estimation of the concentration of HCl evolved during the reaction was described in Chapter 2. This titration method involves addition of water to the reaction mixture, giving a water layer containing the HCl and an organic layer containing the crosslinked polystyrene. After titration, extraction of the organic layer is required so that the crosslinked polystyrene may be precipitated. However, it was shown in Chapter 3 that the results obtained by the titration and ultra-violet spectroscopy methods are in excellent

Table 4.

Concentrations of Reactants in the Polystyrene/D.C.M.B. Condensations.

Series	(D.C.M.B.) (mole/l.)	(Polystyrene) (mole/l.)	($SnCl_4$) (mole/l.)
10	0.298	0.961	0.00451
11	0.596	0.961	0.00451
12	0.894	0.961	0.00451
13	0.149	0.961	0.00451
14	0.298	1.442	0.00451
15	0.298	0.481	0.00451
16	0.298	0.720	0.00451
17	0.298	0.961	0.00902
18	0.298	0.961	0.01353
19	0.298	0.961	0.01804
20	0.298	0.240	0.00451

agreement and so the latter was used for convenience.

Using the experimental techniques described in Chapter 2, quantitative ultra-violet spectra of the crosslinked polystyrenes were obtained and employing the procedure detailed in Chapter 3 for calculating the concentration of HCl evolved from a certain reaction mixture after a known reaction time, the relationship between the number of crosslinks formed and reaction time was determined for each series of concentrations of reactants. This method evaluates the overall number of crosslinks present in a polymer, irrespective of whether the crosslinks are intermolecular or intramolecular.

Typical ultra-violet spectra of polystyrene and a series of

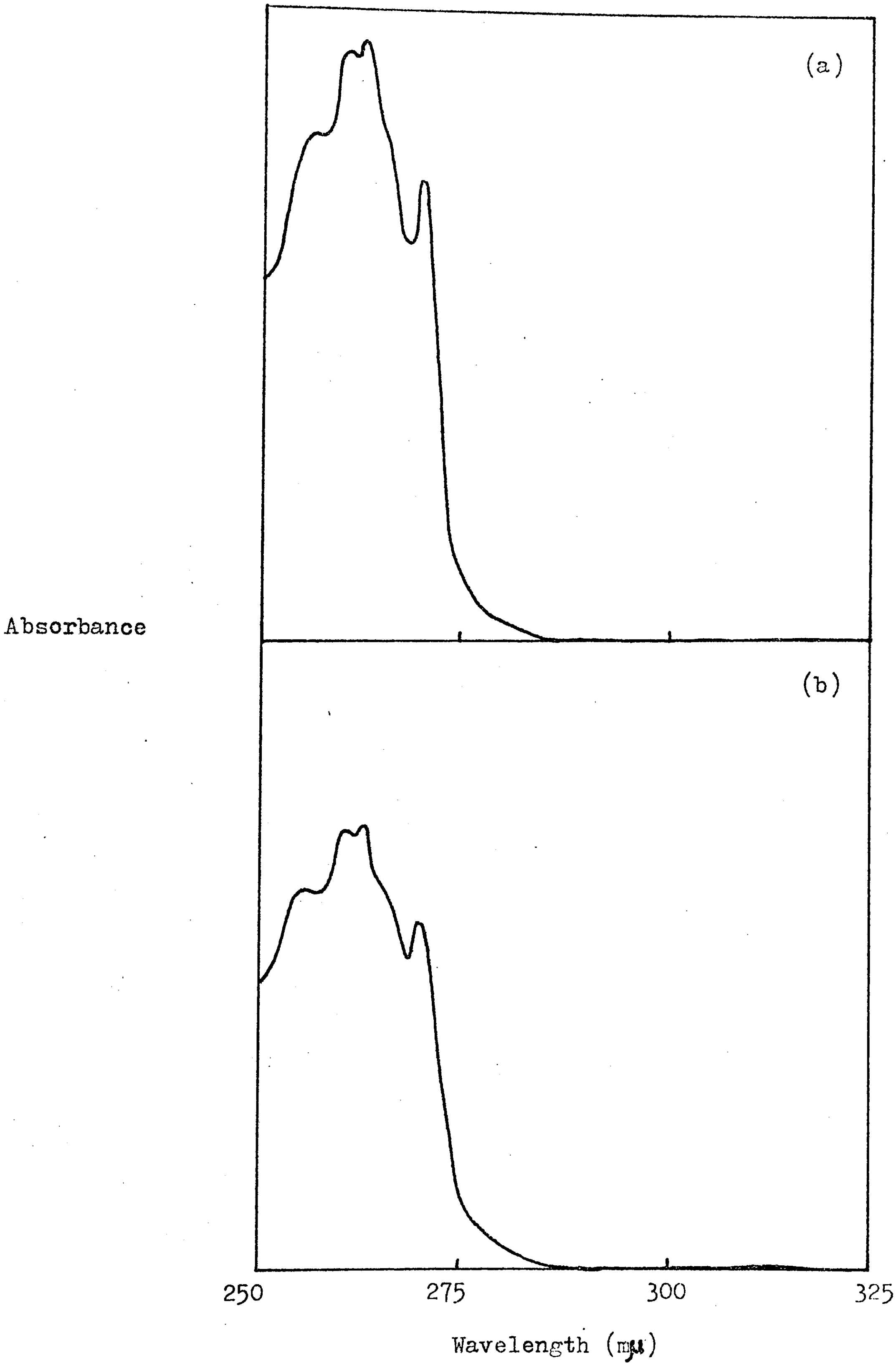


Figure 32. Ultra-violet Spectra of (a) Polystyrene and (b) Polystyrene Crosslinked for 24 hours. (Series 11.)

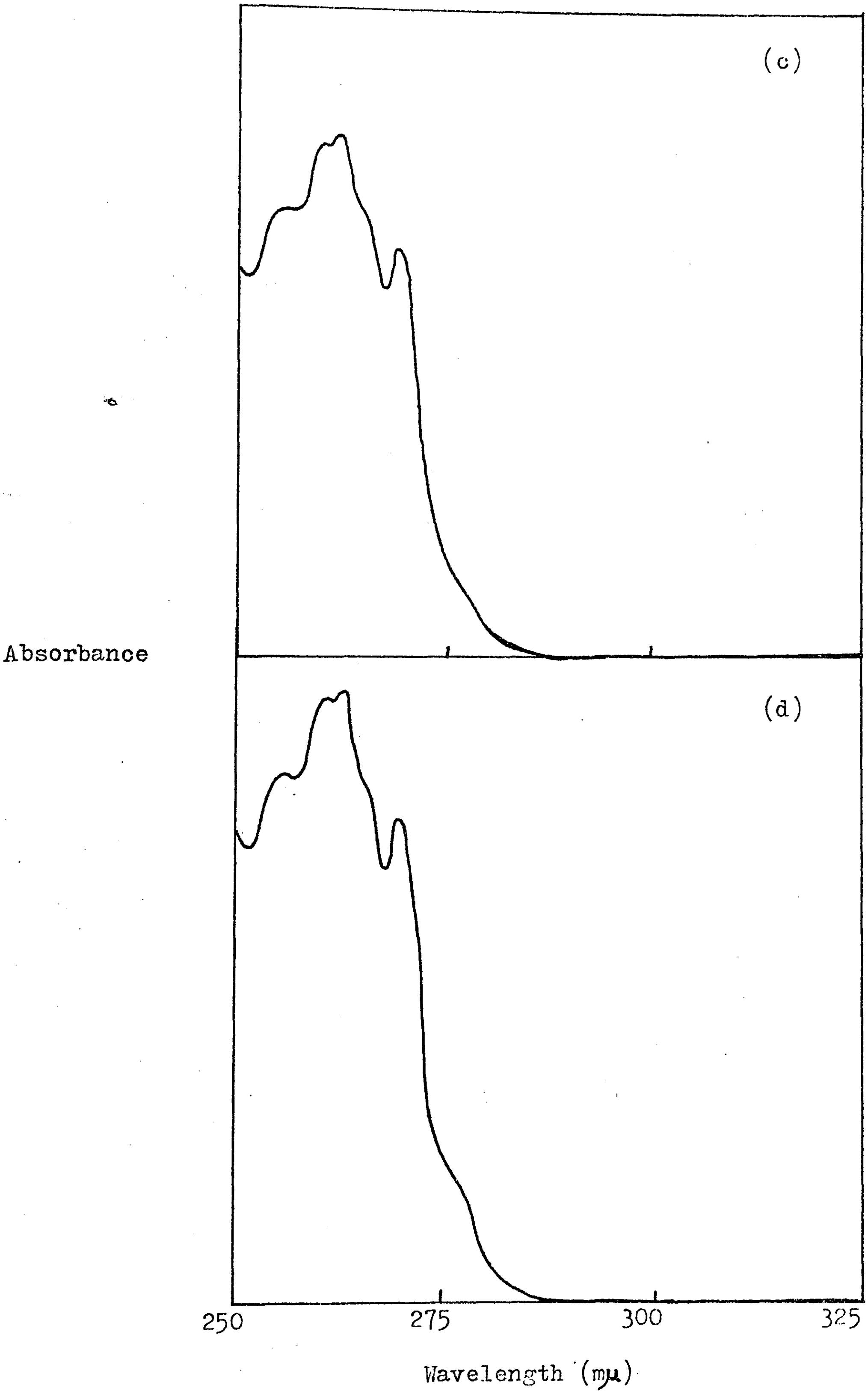


Figure 32. Ultra-violet Spectra of (c) Polystyrene Crosslinked for 42 hours and (d) Polystyrene Crosslinked for 54 hours. (Series 11.)

polystyrenes with an increasing degree of crosslinking are shown in Figure 32. Qualitative examination of these spectra shows that the absorption shoulder at 276mμ, which increases with increasing reaction time, does not appear in the spectrum of polystyrene.

Although intermolecular and intramolecular crosslinking can occur simultaneously and the HCl and ultra-violet methods measure their combined total, only the intermolecular crosslinks increase the molecular weight of the polymer. Thus, in principle, intermolecular and intramolecular crosslinking can be separately measured by a combination of ultra-violet and molecular weight measurements. No direct method is available for determination of the degree of intramolecular crosslinking.

4.4 Kinetics of Crosslinking Polystyrene.

a) Overall Reaction.

Typical plots of HCl evolved, calculated from ultra-violet spectroscopy measurements, versus reaction time are shown in Figure 33. If the value obtained for the concentration of HCl evolved after a certain reaction time is simply halfed, then the concentration of crosslinks per litre of reacting solution may be obtained, since during the evolution of two moles of HCl, one mole of crosslinks are produced. Knowing the concentration of polystyrene in each reaction mixture, the concentration of crosslinks in moles per mole of styrene (N) may be calculated. Using this method the overall concentration of crosslinks in each crosslinked polystyrene sample prepared was calculated from the HCl data listed in Table 8 and the results are presented in Table 5.

The overall concentration of crosslinks, for each series of concentrations of reactants was plotted against reaction time and typical examples are shown in Figure 34. A linear relationship is

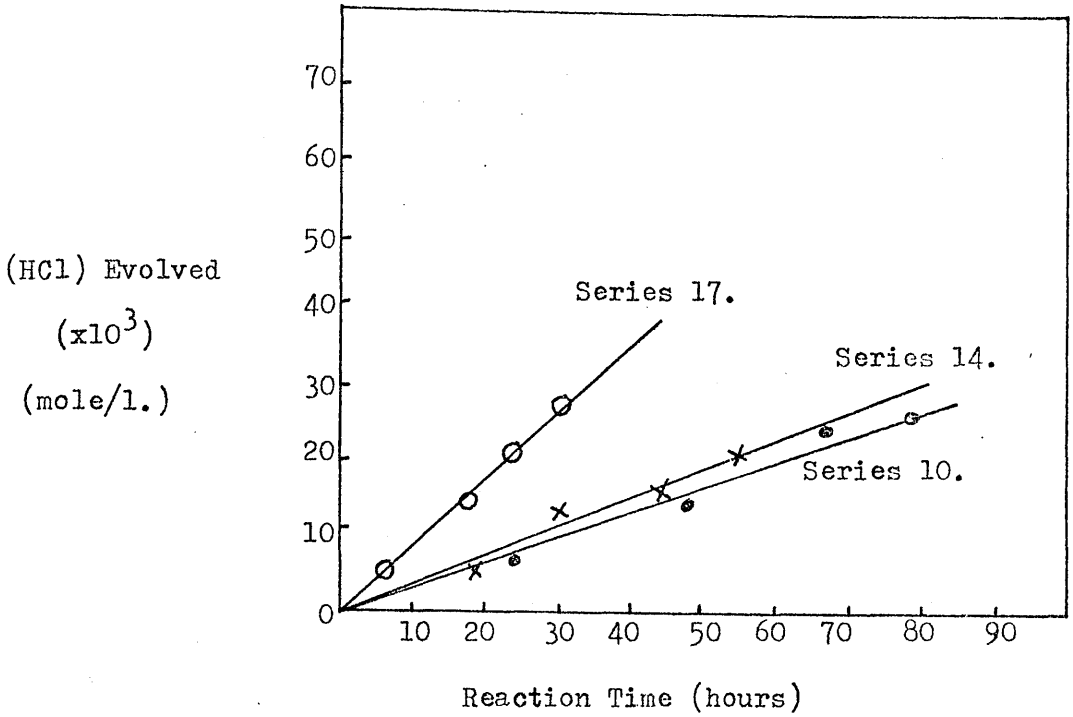


Figure 33. Relationship between HCl Evolution and Reaction Time.

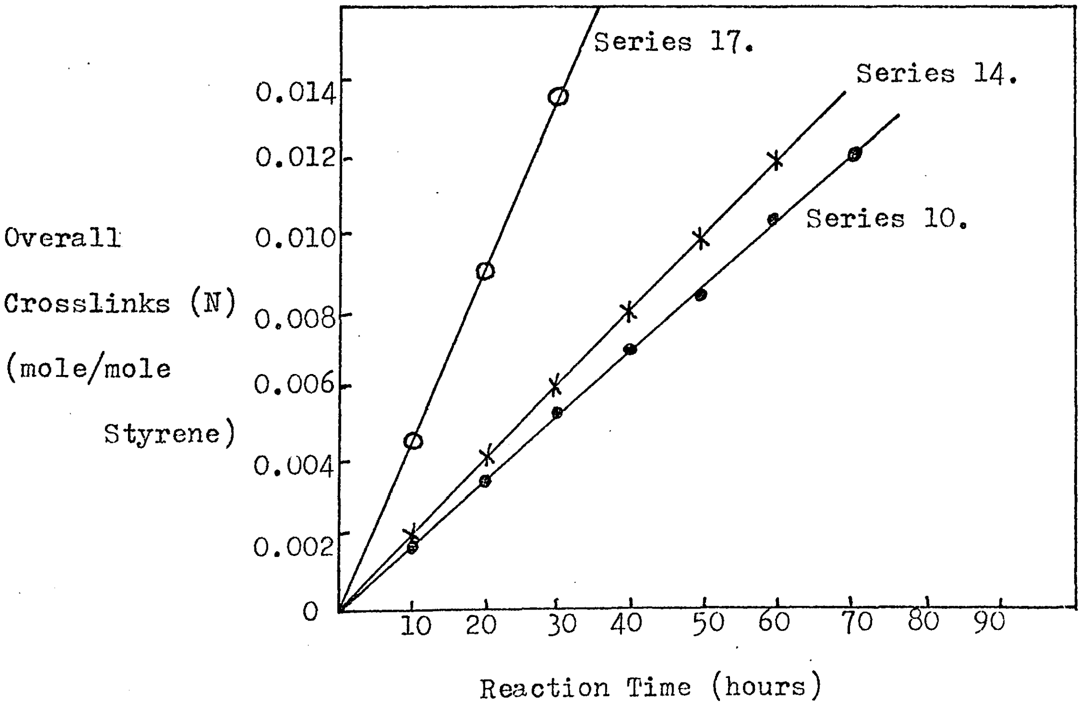


Figure 34. Relationship between Overall Crosslinks and Reaction Time.

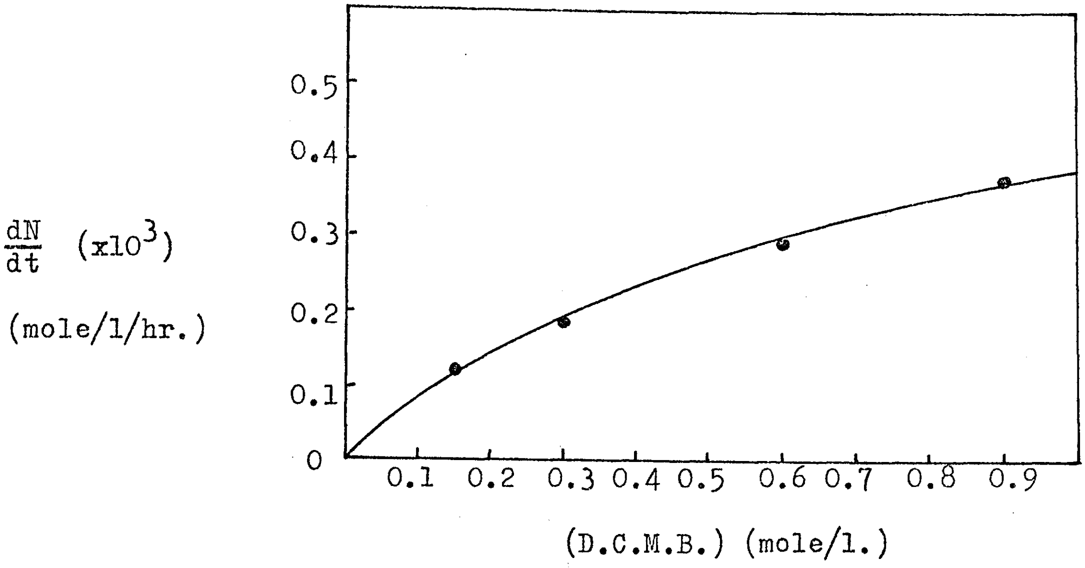


Figure 35. Relationship between Overall Rate of Crosslink Formation and Initial D.C.M.B. Concentration.

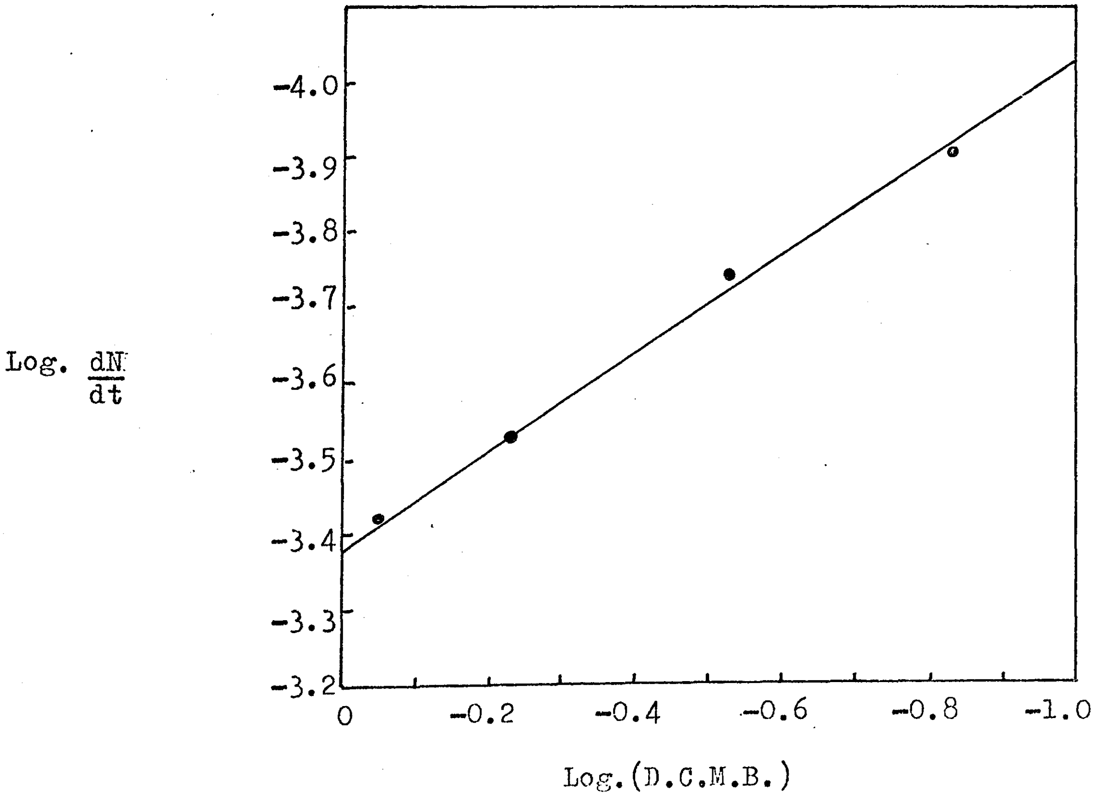


Figure 38. Logarithmic Relationship between Overall Rate of Crosslink Formation and Initial D.C.M.B. Concentration.

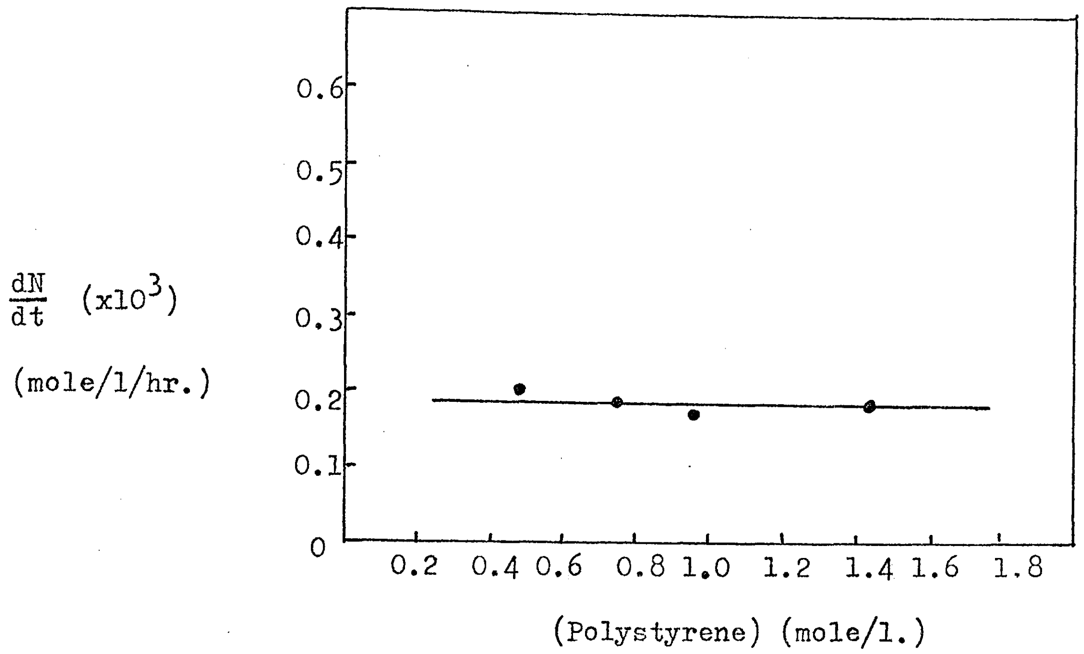


Figure 36. Relationship between Overall Rate of Crosslink Formation and Initial Polystyrene Concentration.

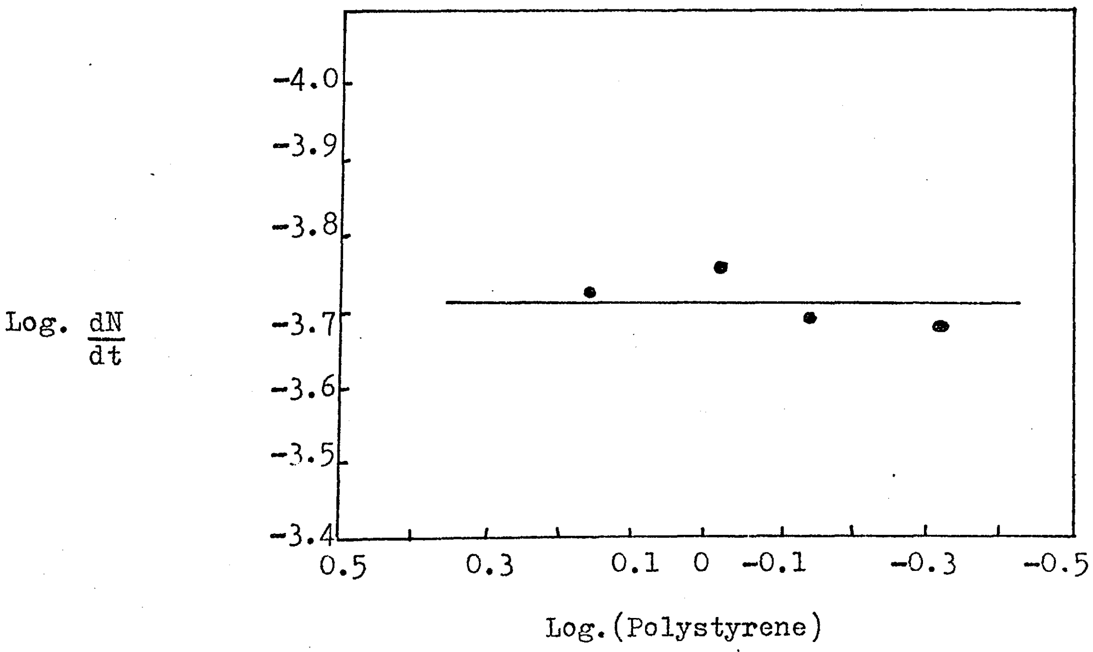


Figure 39. Logarithmic Relationship between Overall Rate of Crosslink Formation and Initial Polystyrene Concentration.

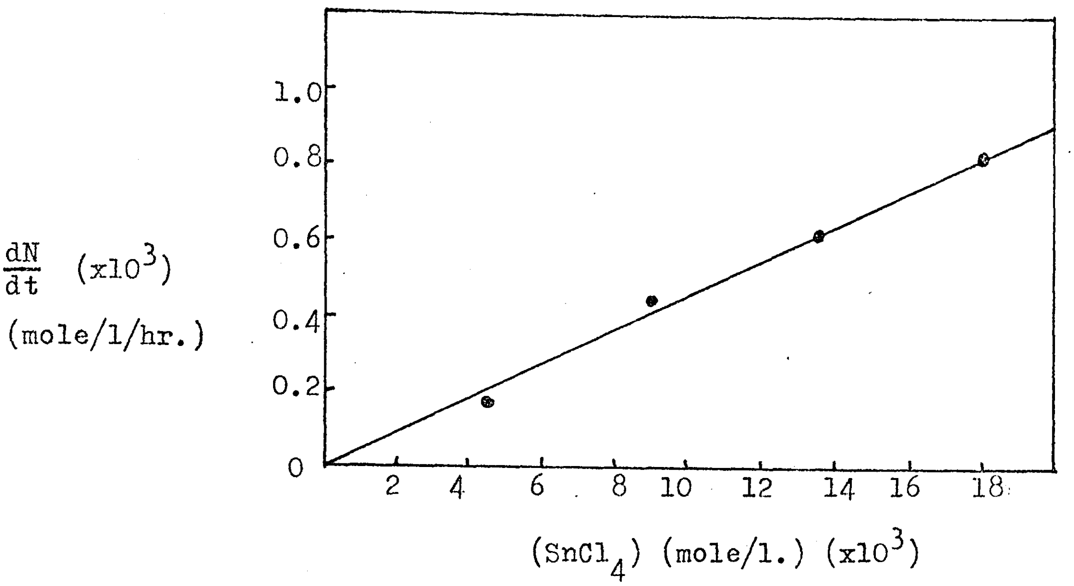


Figure 37. Relationship between Overall Rate of Crosslink Formation and Initial Stannic Chloride Concentration.

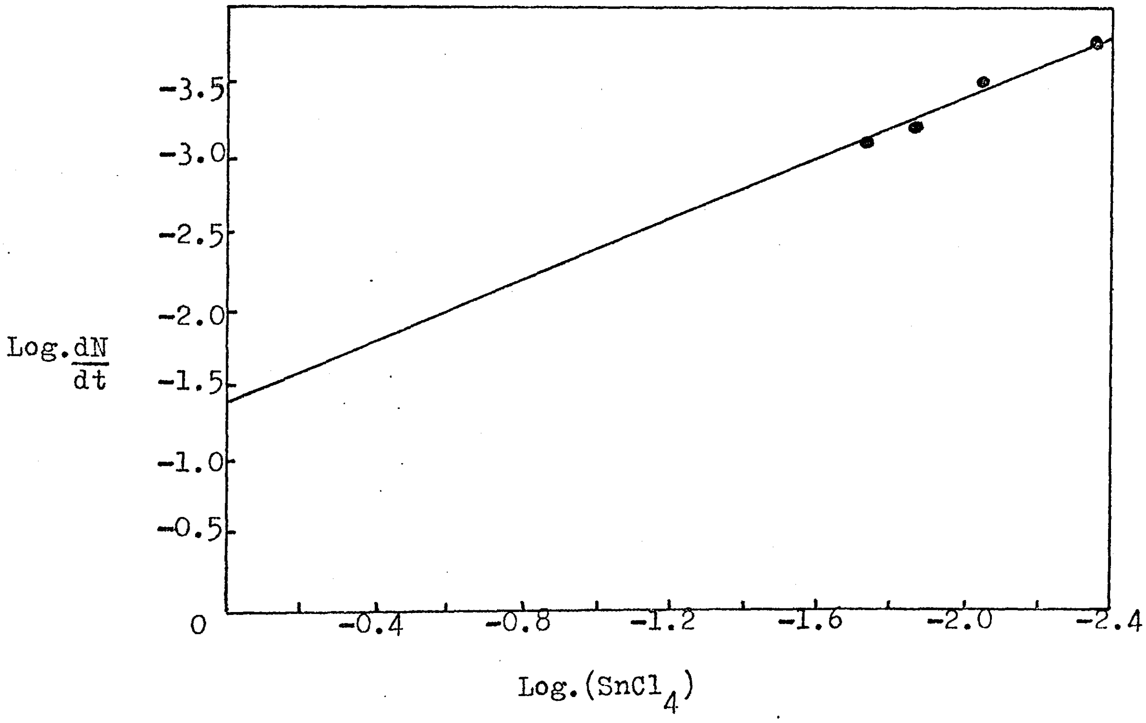


Figure 40. Logarithmic Relationship between Overall Rate of Crosslink Formation and Initial Stannic Chloride Concentration.

Table 5.

Variation of Overall(N), Intermolecular(n) and Intramolecular(N-n) Crosslink Concentration with Reaction Time.

Series	Time (hours)	(Crosslinks) (mole/mole Styrene)		
		N	n	N-n
10	10	0.00175	0.00095	0.0008
10	20	0.0035	0.00169	0.0017
10	30	0.0055	0.00241	0.0027
10	40	0.0070	0.00306	0.0038
10	50	0.0085	0.00356	0.0049
10	60	0.0105	0.00413	0.0062
10	70	0.012	0.00463	0.0075
10	80	0.014	0.00513	0.0093
11	10	0.003	0.00116	0.0018
11	20	0.0058	0.00214	0.0037
11	30	0.0088	0.00306	0.0056
11	40	0.115	0.00384	0.0079
11	50	0.0145	0.00454	0.0100
11	60	0.0175	0.00518	0.0124
12	10	0.00375	0.00086	0.0027
12	20	0.0075	0.00185	0.0055
12	30	0.01125	0.00276	0.0081
12	40	0.015	0.00356	0.0116
12	50	0.019	0.00428	0.0147
12	60	0.0228	0.00444	0.0179

Table 5. (contd.)

Series	Time (hours)	(Crosslinks) (mole/mole Styrene) N	n	N-n
13	10	0.0015	0.00049	0.0007
13	20	0.0028	0.00096	0.0014
13	40	0.0055	0.00185	0.0031
13	50	0.0065	0.00228	0.0037
13	70	0.009	0.00286	0.0057
13	80	0.0103	0.00324	0.0066
13	100	0.0125	0.00378	0.0087
13	110	0.0138	0.00396	0.0100
13	120	0.015	0.0040	0.0110
14	10	0.002	0.00096	0.00090
14	20	0.004	0.00185	0.0019
14	30	0.006	0.00276	0.0031
14	40	0.0078	0.00356	0.0043
14	50	0.0098	0.00437	0.0057
15	20	0.004	0.00074	0.0034
15	40	0.0085	0.00169	0.0067
15	60	0.0125	0.00264	0.0101
15	80	0.017	0.0034	0.0133
15	100	0.021	0.00413	0.0168
15	120	0.025	0.00477	0.0204
15	140	0.0295	0.00533	0.0241

Table 5. (contd.)

Series	Time (hours)	(Crosslinks) (mole/mole Styrene)		
		N	n	N-n
16	20	0.004	0.00153	0.0026
16	40	0.008	0.00286	0.0054
16	60	0.0125	0.0039	0.0084
16	80	0.0165	0.00484	0.0116
16	100	0.0205	0.00566	0.0149
17	10	0.0045	0.00153	0.003
17	20	0.009	0.00264	0.0063
17	30	0.0135	0.00371	0.0097
17	40	0.018	0.00474	0.00133
18	10	0.006	0.00185	0.0044
18	20	0.0125	0.00333	0.0091
18	30	0.0185	0.00459	0.0138
19	5	0.004	0.00135	0.0023
19	10	0.008	0.0024	0.0056
19	15	0.0125	0.0034	0.0080
19	20	0.0165	0.0043	0.0124
19	30	0.0248	0.0057	0.0191

Table 5. (contd.)

Series	Time (hours)	(Crosslinks) (mole/mole Styrene) N	n	N-n
20	20	0.005	0.00026	0.00045
20	40	0.0105	0.00074	0.0009
20	60	0.0155	0.00116	0.0014
20	80	0.021	0.0017	0.0019
20	100	0.027	0.0021	0.0024
20	120	0.032	0.0026	0.00285
20	140	0.037	0.0031	0.00335
20	160	0.043	0.0034	0.0038
20	180	0.048	0.0038	0.0043
20	200	0.053	0.0041	0.0048
20	220	0.058	0.0044	0.0053
20	240	0.063	0.0047	0.00575

Table 6.

Relationship between Rate of Crosslinking and Initial Concentrations of Reactants.

Series	(D.C.M.B.) (mole/l.)	$\frac{dN}{dt}$ (x10^4) (mole/l/hr)	$\frac{dn}{dt}$ (x10^4) (mole/l/hr)	$\frac{d(N-n)}{dt}$ (x10^4) (mole/l/hr)
10	0.298	1.74	1.00	0.80
11	0.596	2.92	1.20	1.70
12	0.894	3.80	1.40	2.80
13	0.149	1.25	0.30	0.60
	(Polystyrene) (mole/l.)			
10	0.961	1.70	1.00	0.80
14	1.442	1.85	1.00	1.00
15	0.481	2.10	0.40	1.80
16	0.720	2.05	0.80	1.20
20	0.24	2.60	0.15	2.40
	($SnCl_4$) (mole/l.)			
10	0.00451	1.70	1.00	0.80
17	0.00902	4.45	1.40	3.10
18	0.01353	6.20	1.80	4.40
19	0.01804	8.20	2.80	5.20

Table 7.

Logarithmic Relationship between Rate of Crosslinking and Initial Reactant Concentrations.

Series	log.(D.C.M.B.)	$\log.\frac{dN}{dt}$	$\log.\frac{dn}{dt}$	$\log.\frac{d(N-n)}{dt}$
10	-0.526	-3.76	-4.00	-4.09
11	-0.225	-3.54	-3.92	-3.77
12	-0.048	-3.42	-3.85	-3.55
13	-0.827	-3.90	-4.53	-4.22
	log.(Polystyrene)			
10	-0.017	-3.77	-4.00	-4.09
14	0.159	-3.73	-4.00	-4.00
15	-0.318	-3.68	-4.40	-3.75
16	-0.142	-3.69	-4.09	-3.92
20	-0.620	-3.59	-4.82	-3.62
	log.($SnCl_4$)			
10	-2.35	-3.77	-4.00	-4.09
17	-2.05	-3.35	-3.85	-3.51
18	-1.87	-3.21	-3.75	-3.36
19	-1.74	-3.09	-3.55	-3.28

Table 8.

Dependence of Molecular Weight and HCl Evolution upon Reaction Time.

Series	Time (hours)	(HCl) ($\times 10^3$) (mole/l.)	$\overline{M}_n$ ($\times 10^{-4}$)	log.$\overline{M}_n$
10	24	6.7	2.08	4.32
10	48	13.6	2.49	4.39
10	66	28.0	3.50	4.54
10	78	28.0	4.02	4.60
11	24	11.8	2.25	4.35
11	42	25.4	2.92	4.47
11	54	31.2	3.76	4.58
12	24	20.6	2.30	4.36
12	42	30.0	2.63	4.42
12	54	39.2	3.20	4.51
13	30	8.5	1.50	4.18
13	66	16.8	2.10	4.32
13	100	25.2	2.92	4.47
14	18	6.4	1.82	4.26
14	30	15.2	2.42	4.38
14	44	14.8	2.73	4.44
14	54	21.4	3.70	4.57
15	72	30.4	2.30	4.36
15	114	48.0	3.52	4.55
15	144	61.0	5.07	4.71

Table 8. (contd.)

Series	Time (hours)	(HCl) ($\times 10^3$) (mole/l.)	$\bar{M}_n$ ($\times 10^{-4}$)	log.$\bar{M}_n$
16	24	10.0	1.91	4.28
16	54	22.0	2.77	4.44
16	78	31.8	3.82	4.58
16	96	38.8	5.21	4.72
17	6	6.0	1.55	4.19
17	18	13.8	2.05	4.31
17	24	21.0	2.30	4.36
17	30	28.6	2.66	4.43
18	18	18.8	2.34	4.36
18	24	30.0	2.80	4.45
18	27	36.8	3.09	4.49
19	6	8.0	1.80	4.26
19	18	33.2	2.68	4.43
19	20	30.2	3.34	4.52
20	96	61.4	2.06	4.31
20	144	75.0	2.41	4.38
20	192	85.6	2.88	4.46
20	240	126.0	3.57	4.55

obtained, the gradient representing the rate of formation of overall crosslinks. By varying the concentration of each reactant in turn, while maintaining the other two constant and by plotting the rate of formation of the overall number of crosslinks against the initial concentration of each reactant, the graphs shown in Figures 35, 36 and 37 were obtained, from the values presented in Table 6.

The graph of the rate of overall crosslink formation $\left(\frac{dN}{dt}\right)$ versus the initial D.C.M.B. concentration is a curve, as shown in Figure 35 and in order to determine the order of the reaction with respect to the initial D.C.M.B. concentration, it was necessary to plot the corresponding logarithmic relationship as shown in Figure 38. The gradient of this linear plot which is the order of the reaction with respect to the D.C.M.B. concentration, is 0.65.

By plotting the rate of overall crosslink formation against the initial polystyrene concentration, a straight line parallel to the concentration axis is obtained, as shown in Figure 36. This indicates that the rate of overall crosslink formation is independent of the initial polystyrene concentration and, therefore, the order of the reaction with respect to the polystyrene concentration is zero, over the concentration range studied. The corresponding logarithmic plot, shown in Figure 39, verifies the above observation.

As the graph of the rate of overall crosslink formation versus the initial stannic chloride concentration gives a straight line passing through the origin, as shown in Figure 37, the order of the crosslinking reaction with respect to the stannic chloride concentration is unity. A plot of the corresponding logarithmic relationship, as shown in Figure 40, gives a linear relationship of unit gradient confirming this. The values used in these logarithmic plots are presented in Table 7.

The overall reaction may thus be represented by the rate equation,

$$\frac{dN}{dt} = k_N(\text{D.C.M.B.})^{0.65}(\text{Polystyrene})^0(\text{SnCl}_4)$$

or $$\log.\frac{dN}{dt} = \log.k_N + 0.65 \log.(\text{D.C.M.B.}) + \log.(\text{SnCl}_4)$$

The average value of the rate constant, k_N, at 30°C, obtained from a large amount of rate versus concentration data is,

$$k_N = 2.5 \times 10^{-5} \text{ l.mole.}^{-1}\text{s.}^{-1}$$

b) Intermolecular Reaction.

The number average molecular weight ($\bar{M}_n$) of each polymer was measured in order to determine the variation in intermolecular crosslinks with reaction time. Typical plots of $\bar{M}_n$ versus reaction time are shown in Figure 41, and the linear plots obtained in the corresponding graphs of $\log.\bar{M}_n$ against reaction time, shown in Figure 42 indicate that the increase in $\bar{M}_n$ with reaction time is exponential. Data are collected in Table 8. From these data, the concentration of intermolecular crosslinks in a given polymer may be calculated as follows.

If m is the number of intermolecular crosslinks formed per initial molecule and M_o and M_t are the chain lengths at times zero and t, respectively, then it follows that,

$$M_t = \frac{M_o}{1 - m}$$

$$1 - m = \frac{M_o}{M_t}$$

$$m = 1 - \frac{M_o}{M_t}$$

If n is the number of intermolecular crosslinks per monomer unit (moles/mole styrene) then,

$$n = \frac{m}{M_o}$$

$$= \frac{1}{M_o} - \frac{1}{M_t}$$

$$= \frac{M_t - M_o}{M_t M_o}$$

Thus, knowing the molecular weight of a crosslinked polymer, the concentration of intermolecular crosslinks may be easily determined.

Values of n obtained in this way are presented in Table 5 and plotted in Figure 43. It can be seen that the relationship between the concentration of intermolecular crosslinks and reaction time is not linear since their rate of formation decreases as the gel point is approached. However, as it is the initial stages of the reaction which are under investigation, the rate of formation of intermolcecular crosslinks for each series of reactant concentrations may be determined by assuming the initial section of the curve to be linear. The rates of formation of intermolecular crosslinks, measured in this way, for each series of concentrations of reactants are presented in Table 6.

Graphs of the rates of formation of intermolecular crosslinks $\left(\frac{dn}{dt}\right)$ versus initial D.C.M.B., polystyrene and stannic chloride concentrations, are shown in Figures 44, 45 and 46, respectively. In each case a linear relationship, passing through the origin is obtained

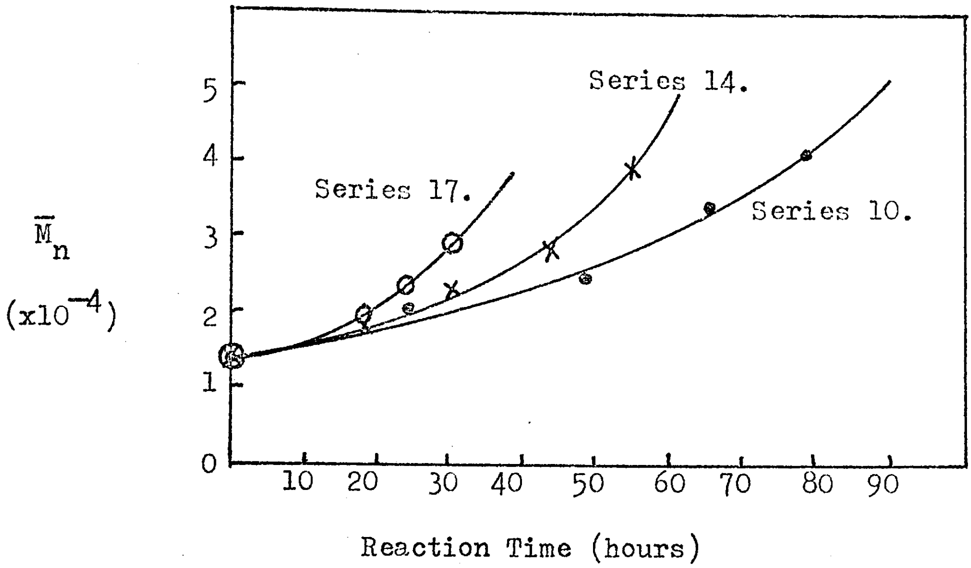


Figure 41. Relationship between Molecular Weight and Reaction Time.

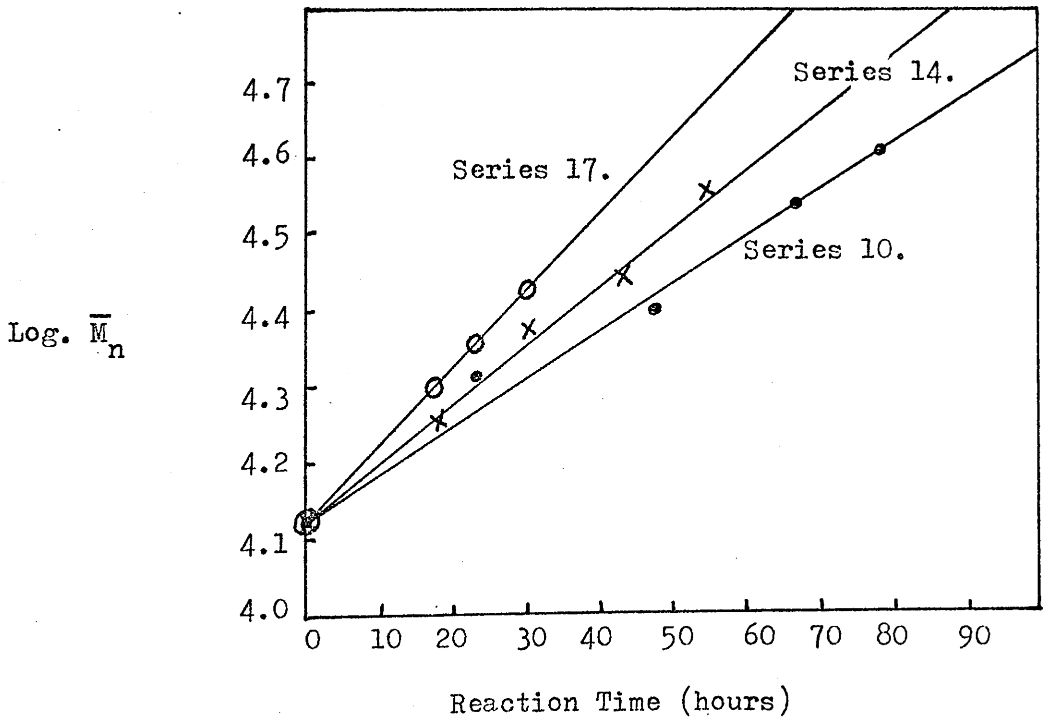
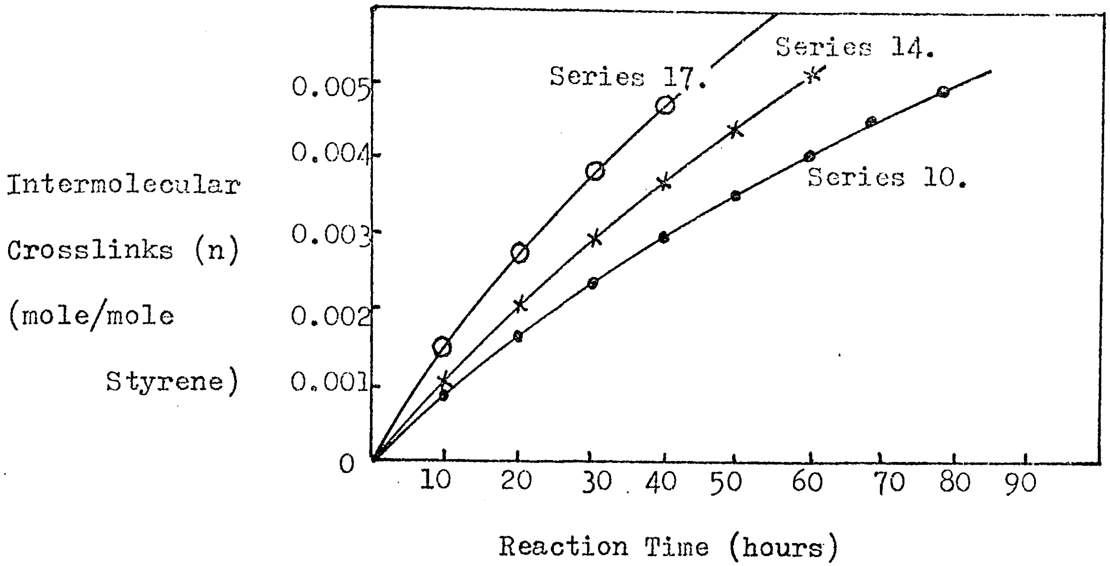
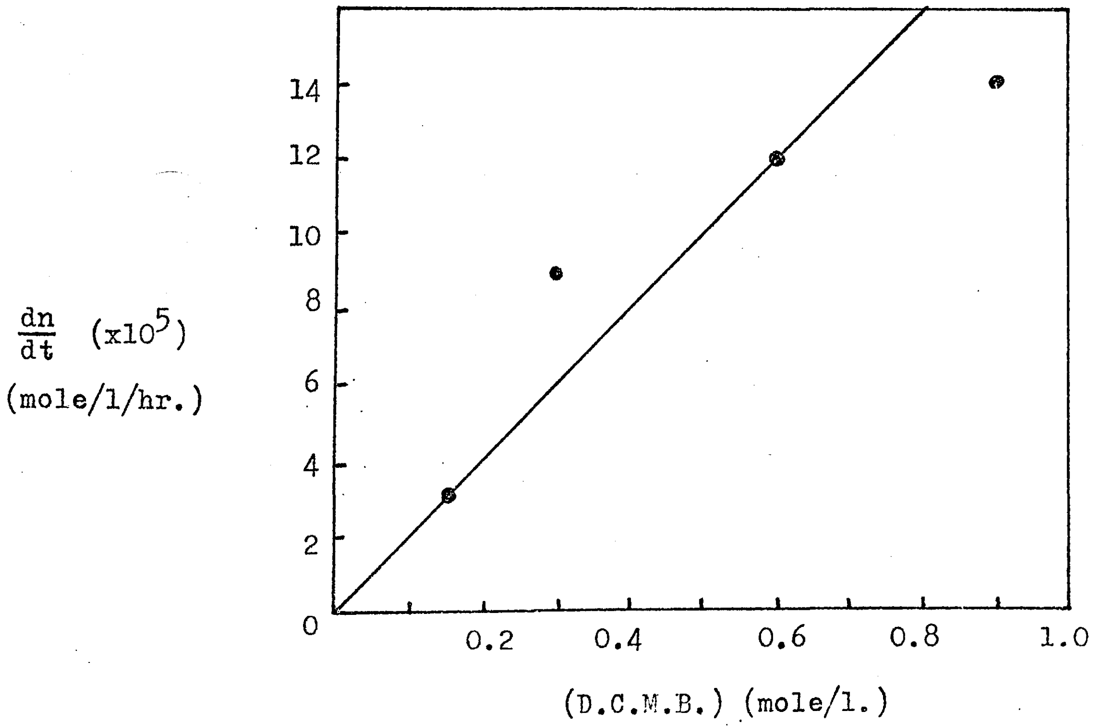


Figure 42. Logarithmic Relationship between Molecular Weight and Reaction Time.



<u>Figure 43</u>. Relationship between Intermolecular Crosslinks and Reaction Time.



<u>Figure 44</u>. Relationship between Rate of Intermolecular Crosslink Formation and Initial D.C.M.B. Concentration.

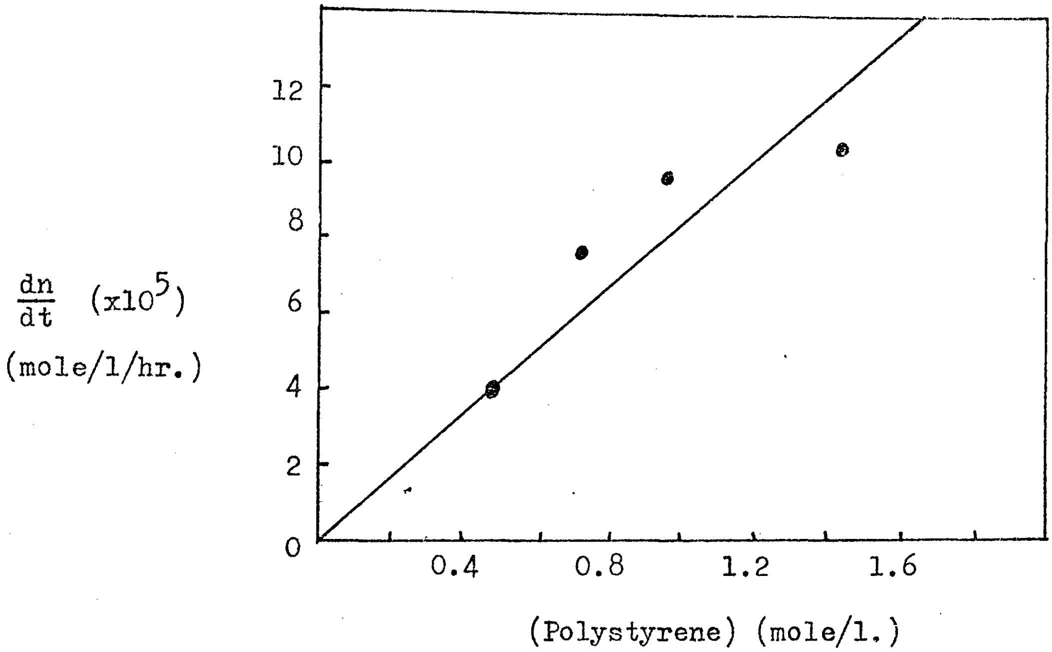


Figure 45. Relationship between Rate of Intermolecular Crosslink Formation and Initial Polystyrene Concentration.

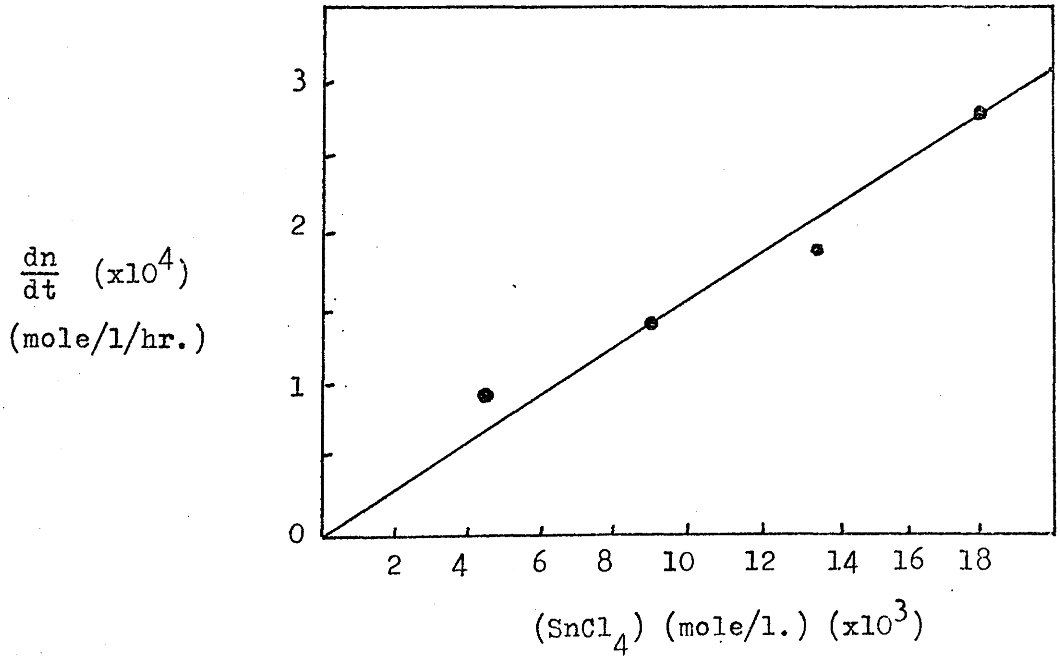


Figure 46. Relationship between Rate of Intermolecular Crosslink Formation and Initial Stannic Chloride Concentration.

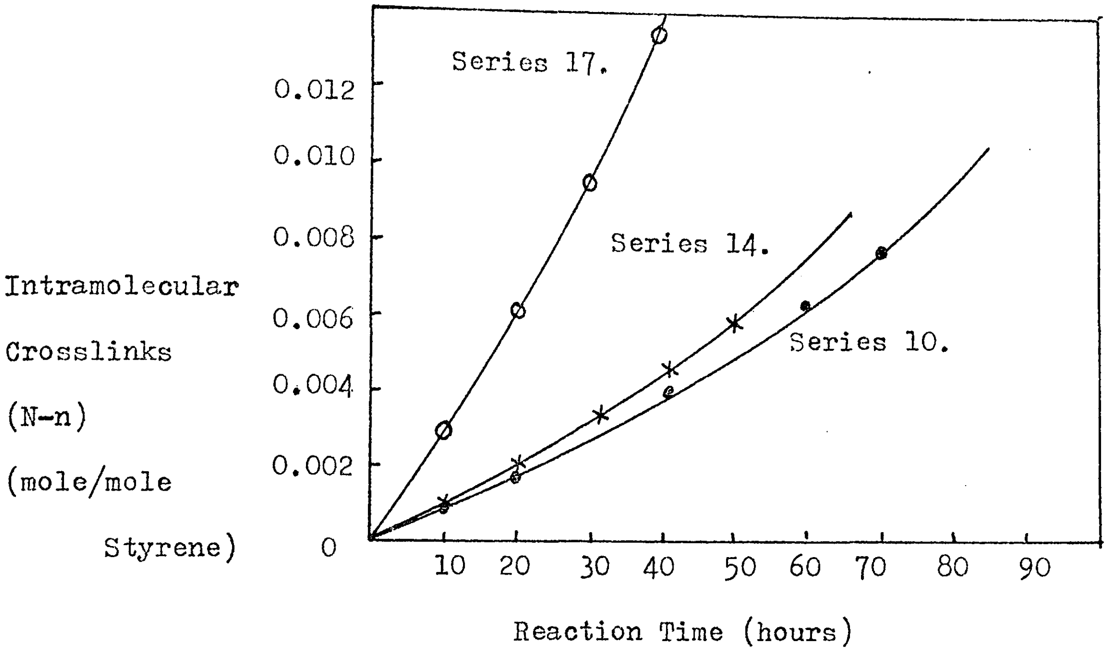


Figure 47. Relationship between Intramolecular Crosslinks and Reaction Time.

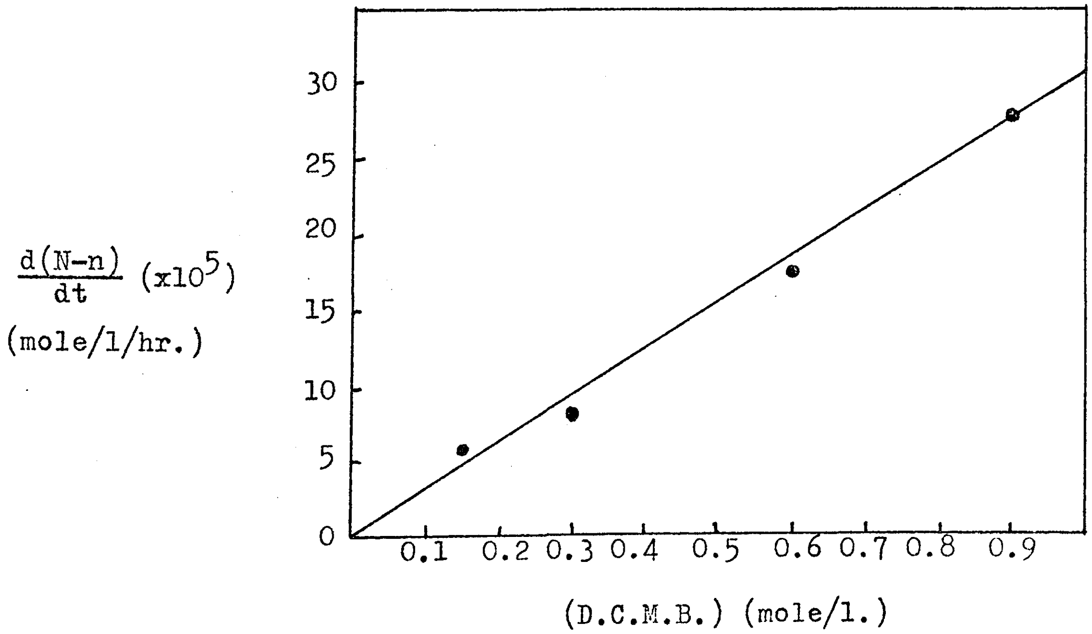


Figure 48. Relationship between Rate of Intramolecular Crosslink Formation and Initial D.C.M.B. Concentration.

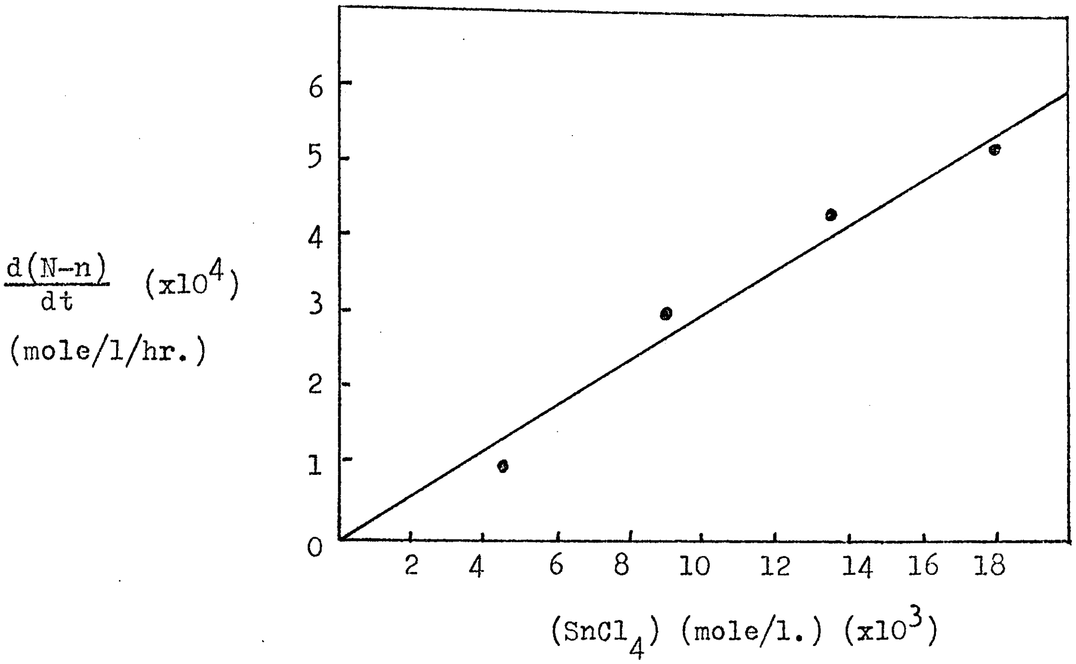


Figure 49. Relationship between Rate of Intramolecular Crosslink Formation and Initial Stannic Chloride Concentration.

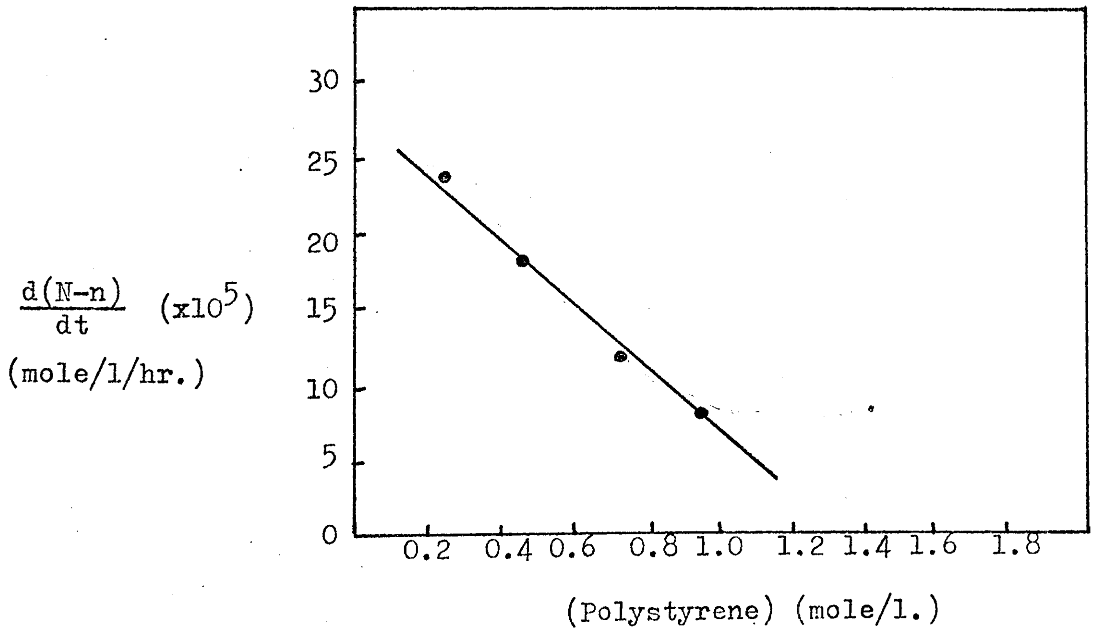


Figure 50. Relationship between Rate of Intramolecular Crosslink Formation and Initial Polystyrene Concentration.

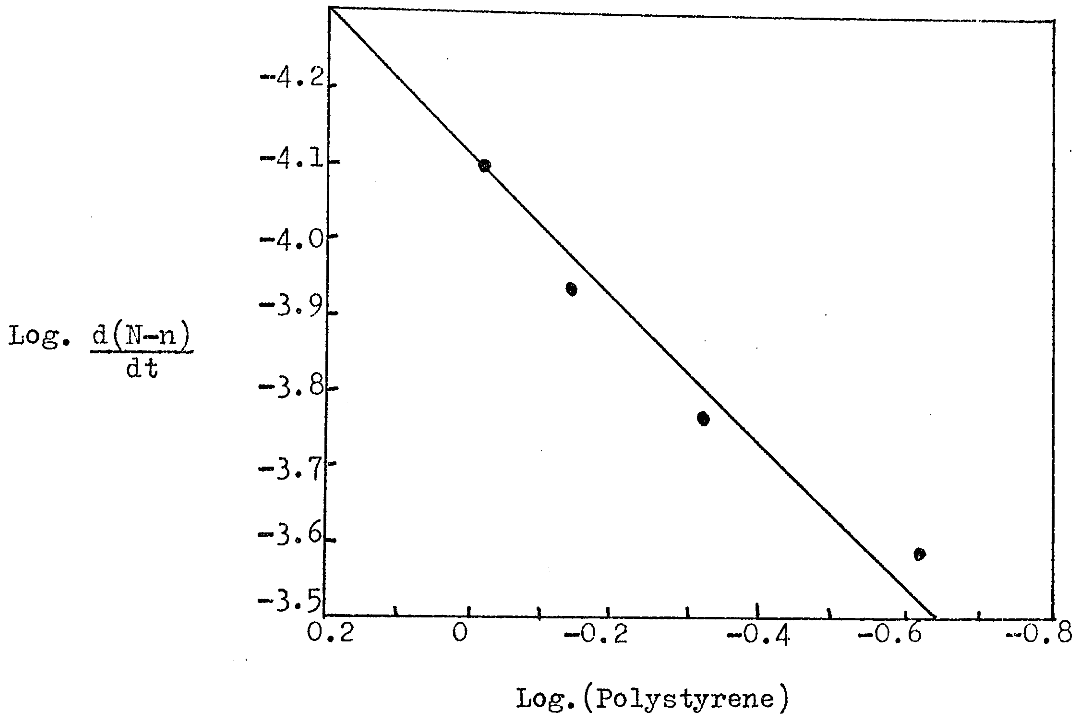


Figure 51. Logarithmic Relationship between Rate of Intramolecular Crosslinking and Initial Polystyrene Concentration.

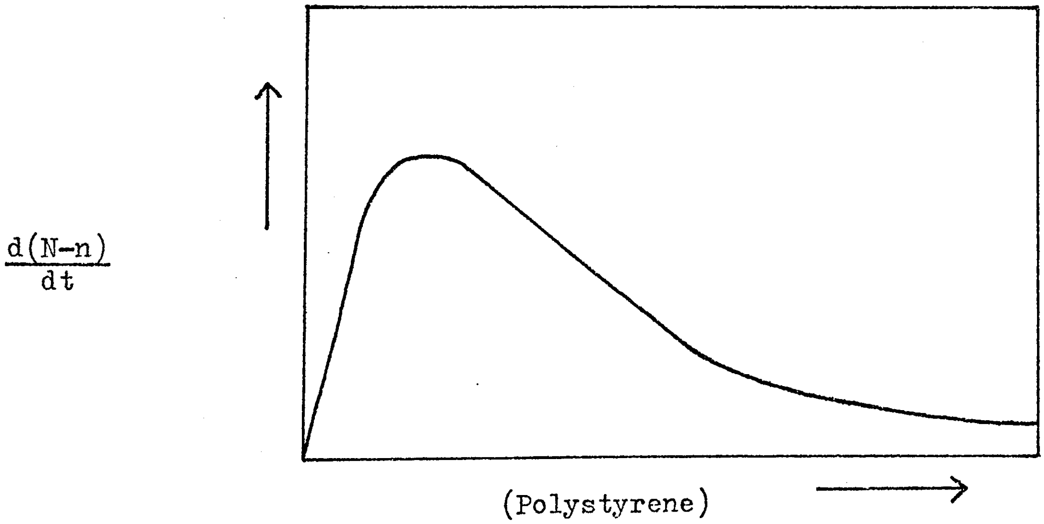


Figure 52. Postulated Relationship between Rate of Intramolecular Crosslinking and Initial Polystyrene Concentration.

showing that the order of the intermolecular crosslinking reaction, with respect to the initial concentration of each reactant, is unity.

Thus the rate equation for the intermolecular crosslinking reaction is,

$$\frac{dn}{dt} = k_n(\text{D.C.M.B.})(\text{Polystyrene})(\text{SnCl}_4)$$

and evaluation of the rate constant (k_n) at 30°C gives,

$$k_n = 0.725 \times 10^{-5} \ \text{l}^2\text{.mole.}^{-2}\text{s.}^{-1}$$

c) Intramolecular Reaction.

As the relationships between the overall concentration of crosslinks and reaction time and the concentration of the intermolecular crosslinks and reaction time are now known, for each series of concentrations of reactants, the relationship between the concentration of intramolecular crosslinks (N - n) (mole/mole Styrene) and reaction time is available, by difference. Figure 47 shows the relationship between the concentration of intramolecular crosslinks and reaction time, obtained from the values listed in Table 5. It can be seen that the rate of formation of intramolecular crosslinks is slow in the initial stages of the reaction but increases as the gel point is approached. As in the intermolecular reaction it is the initial stages of the reaction which are of interest, for the purposes of a kinetic investigation, and so the rate of change of the concentration of intramolecular crosslinks was obtained from the initial linear portion of the curve. The values obtained for these initial rates are presented in Tables 6 and 7.

Figures 48 and 49 show the relationship between the rate of intramolecular crosslink formation and the initial concentrations of D.C.M.B. and stannic chloride, respectively. As a straight line passing through the origin is obtained, in each case, the reaction is first order with respect to the concentrations of these two reactants.

The graph obtained for the variation in the rate of intramolecular crosslink formation with the initial polystyrene concentration is rather unusual and is shown in Figure 50. The corresponding logarithmic plot, shown in Figure 51, has a gradient of -1. This means that the rate of intramolecular crosslink formation, in the initial stages of the reaction, decreases with increasing polystyrene concentration, with the result that the order of the reaction with respect to the initial polystyrene concentration is -1. As the polystyrene concentration is increased, the intramolecular reaction is presumably inhibited since the molecules become more coiled, inhibiting the diffusion of the reagents into the coils. At extremely low polystyrene concentrations, the rate of intramolecular crosslinking will increase since the molecules will be more rod-like and a greater proportion of the aromatic rings will thus be vulnerable to reaction. As the graph of the rate of intramolecular crosslink formation versus the initial polystyrene concentration must pass through the origin, the complete graph must be of the form shown in Figure 52. It can be seen that the rate of the reaction must increase initially, followed by the main linear portion of the curve, described in detail above, and finally as the rate of the reaction can never be negative, the curve must 'tail off' at high polystyrene concentrations. A consequence of these predictions is that there must be a certain polystyrene concentration at which the rate of intramolecular crosslinking is at a maximum.

The rate equation for the intramolecular reaction may be written as,

$$\frac{d(N-n)}{dt} = k_{N-n}\frac{(D.C.M.B.)(SnCl_4)}{(Polystyrene)}$$

and from the data collected, the rate constant (k_{N-n}) at 30°C was calculated to be,

$$k_{N-n} = 0.675 \times 10^{-5} \text{ s.}^{-1}$$

d) Discussion.

The kinetics of the crosslinking reactions having now been determined, it is necessary to try to reconcile the apparent inconsistencies.

The order of the crosslinking reaction, whether the overall reaction or the separate intermolecular and intramolecular reactions was always unity with respect to the stannic chloride concentration as expected by comparison with the D.C.M.B./$SnCl_4$/benzene, diphenyl methane and thiophene systems.[16,19,24]

However, the order of the overall reaction with respect to the initial polystyrene concentration was found to be zero but the orders of the intermolecular and intramolecular reactions, with respect to the polystyrene concentration were found to be 1 and -1, respectively. The order of the intermolecular reaction requires no explanation and the order of the intramolecular reaction has been discussed in the previous section. If the two reactions are superimposed, then it is reasonable to assume that the orders of the reactions will cancel and give a resultant zero order for the overall reaction. A low order for the autoxidation of polystyrene, with respect to the polystyrene concentration, has similarly been observed.[97] As the concentration of the polystyrene increases, the amount of coiling in the chains increases. The diffusion of the other reactants into these highly coiled molecules becomes more difficult and so the rate of diffusion decreases as the polystyrene concentration increases. Thus the reaction rate does not increase with increasing polystyrene concentration. Consequently, it may be assumed that at low polystyrene concentrations, the intramolecular reaction is predominant and at higher concentrations the intermolecular reaction predominates due to the relative differences in the ease of collision between reacting molecules.

Both the intermolecular and intramolecular reactions have been shown to be first order with respect to the D.C.M.B. concentration. As the overall and intermolecular reaction orders were determined independently and the intramolecular reaction order was calculated by a method which is dependent upon the concentrations of both overall and intermolecular crosslinks, it follows that the order of the overall reaction should also be unity, with respect to the D.C.M.B. concentration and not 0.65 as determined experimentally.

Figure 53 shows the relationship between the rate of the overall crosslinking reaction and the initial D.C.M.B. concentration. These points are identical to those shown in Figure 35, in which it was assumed that the origin must be a point, to obtain the curve shown. In Figure 53 it can be seen that a straight line can be drawn through these same points but that an intercept of,

$$\frac{dN}{dt} = 0.07 \times 10^{-3} \text{ mole.l.}^{-1}\text{s.}^{-1}$$

is obtained on extrapolation. This suggests that another reaction may be occurring with a rate of 0.07×10^{-3} mole.l.$^{-1}$s.$^{-1}$ and this would mean

Table 9.

Postulated Relationship between Rate of Overall Crosslink Formation and Initial D.C.M.B. Concentration.

Series	(D.C.M.B.) (mole/l.)	Intercept $(\times 10^4)$ (mole/l/hr)	Overall Crosslinking Rate (mole/l/hr)	
			Observed $\frac{dN}{dt}$ $(\times 10^4)$	Postulated $\frac{dN^*}{dt}$ $(\times 10^4)$
10	0.298	0.07	1.74	1.04
11	0.596		2.92	2.22
12	0.894		3.80	3.10
13	0.149		1.25	0.55

that the variation in the rate of the overall crosslinking reaction with the initial D.C.M.B. concentration would give the graph shown in Figure 54, obtained by subtracting the intercept value from the rates plotted in Figure 53, as shown in Table 9. If this hypothesis is true then the overall reaction would be first order with respect to the initial D.C.M.B. concentration. The rate equation would be,

$$\frac{dN^*}{dt} = k_N{}^*(\text{D.C.M.B.})(\text{SnCl}_4)$$

and the rate constant ($k_N{}^*$) at 30°C would be,

$$k_N{}^* = 1.50 \times 10^{-5} \text{ l.mole.}^{-1}\text{s.}^{-1}$$

However, no experimental evidence for this hypothetical reaction was obtained but as the predicted reaction rate is extremely low, it is

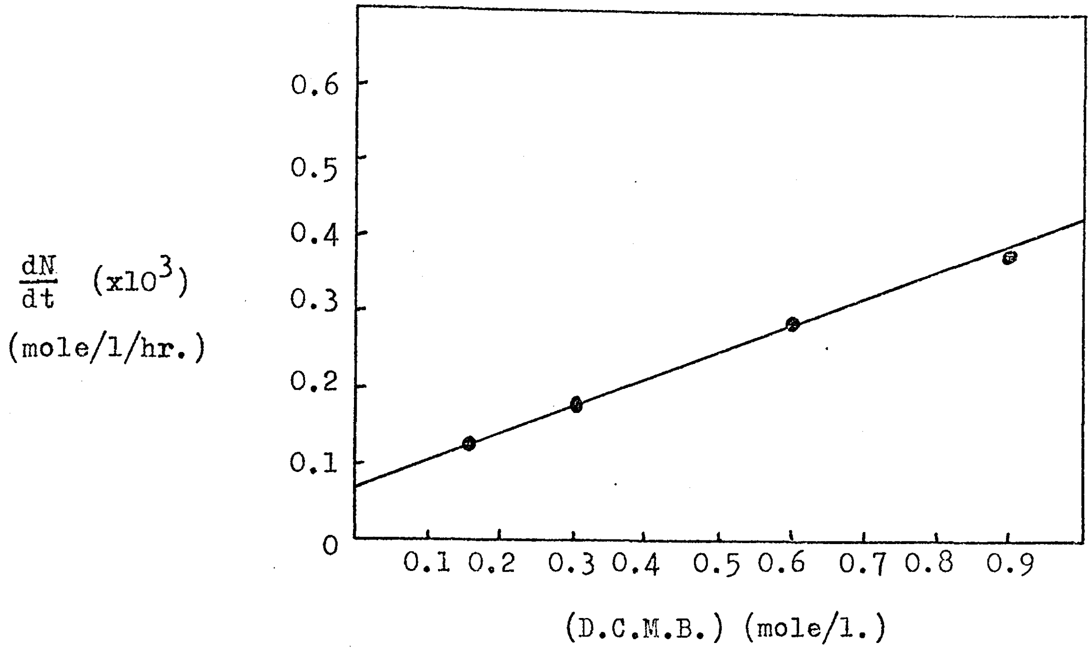


Figure 53. Relationship between Overall Rate of Crosslink Formation and Initial D.C.M.B. Concentration.

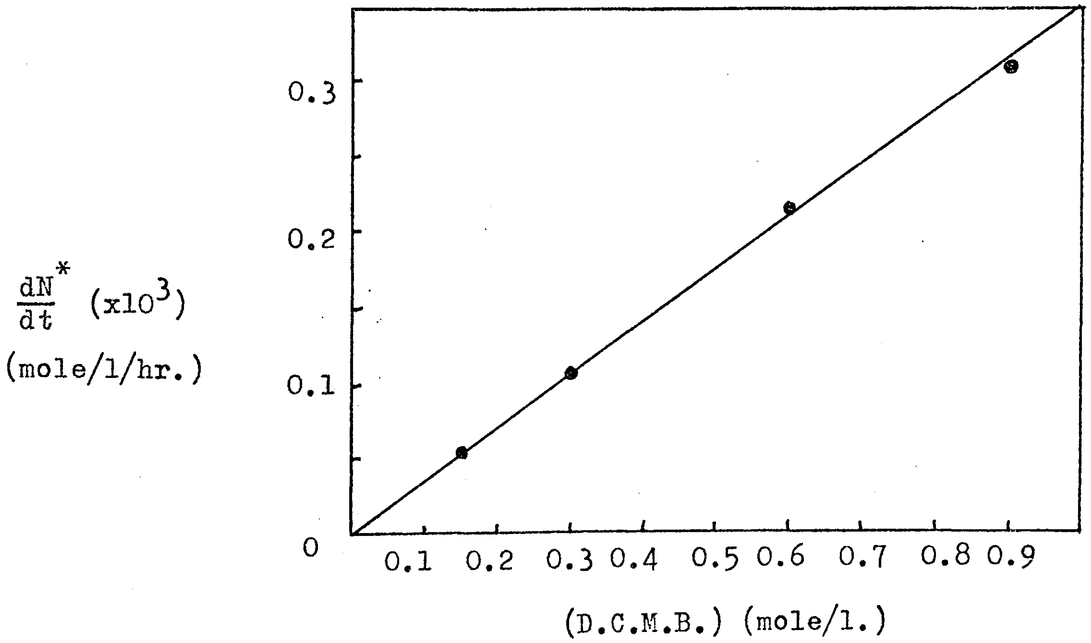


Figure 54. Postulated Relationship between Overall Rate of Crosslink Formation and Initial D.C.M.B. Concentration.

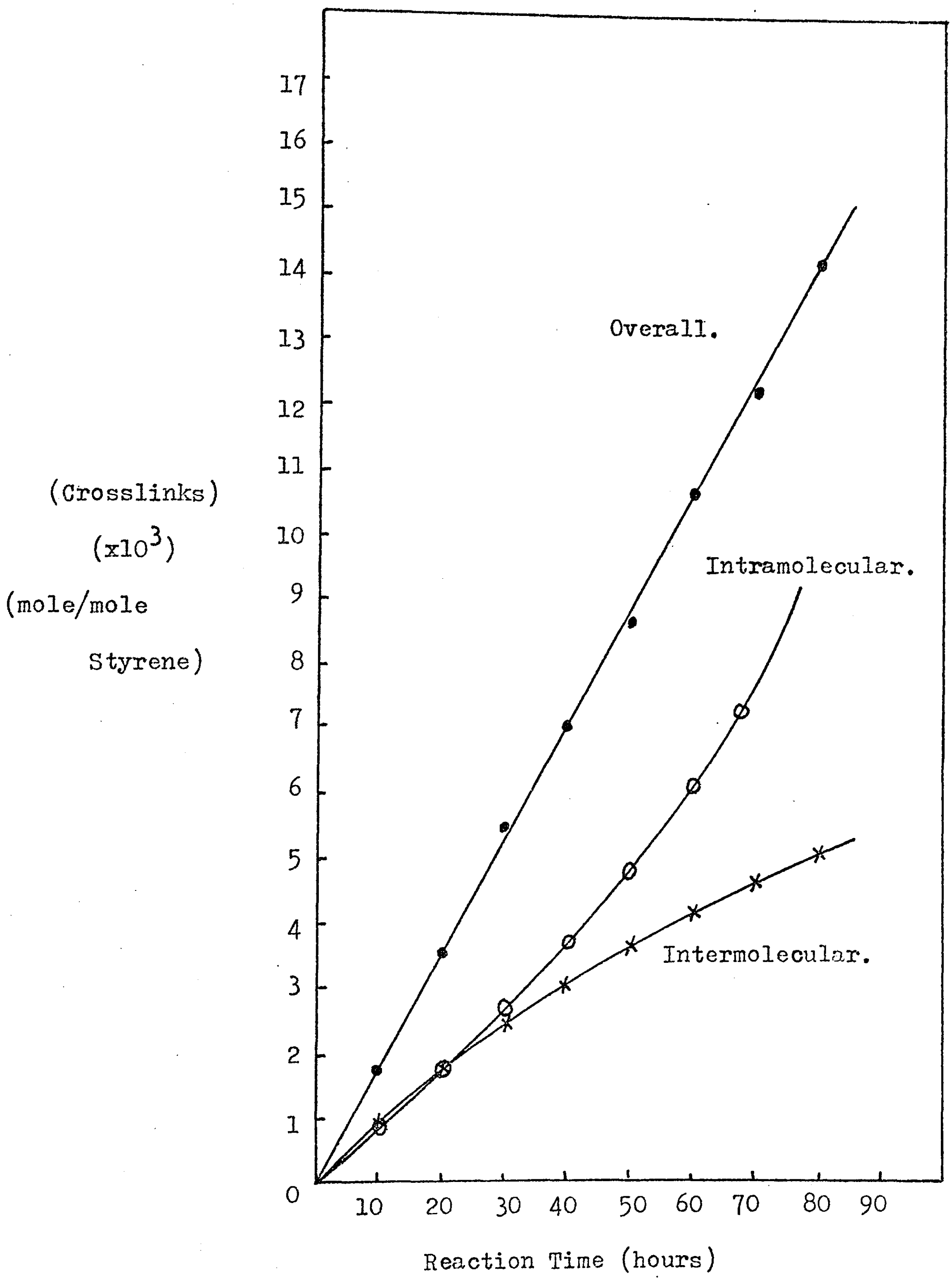


Figure 55. Comparison of the Relationships between the Overall, Intermolecular and Intramolecular Crosslinks with Reaction Time. (Series 10.)

possible that it could not be detected within the accuracy of the techniques employed.

It has been shown that the rate constants for the intermolecular and intramolecular reactions are,

$$k_n = 0.725 \times 10^{-5}\ l.^2 mole.^{-2} s.^{-1}$$

and

$$k_{N-n} = 0.675 \times 10^{-5}\ s.^{-1}$$

The corrected rate constant for the overall reaction (k_N*) derived above, is within experimental error, the sum of these, as would be expected and the slight difference is probably due to the slight effect that the corrected rates of the overall reaction would have on the rates of the intramolecular reaction. The rate constant for the overall reaction, however, was originally found to be,

$$k_N = 2.50 \times 10^{-5}\ l.mole.^{-1} s.^{-1}$$

which is well outwith the range of experimental error, since no correction is necessary and so this gives even more support to the theory of the undetected competing reaction.

The relationship between the concentrations of the overall, intermolecular and intramolecular crosslinks with reaction time, for a series of concentrations of reactants, is shown in Figure 55. The rates of the intermolecular and intramolecular reactions were obtained by assuming the initial portion of the curves to be linear and thus calculating their gradients. Although the rate of the overall reaction can be obtained directly from the linear relationship shown in the upper line in Figure 55, the points on this line were extrapolated to zero to obtain the initial portion of the line, since measurement of the concentration of crosslinks after short reaction times is not sufficiently accurate. It may be that the gradient of the line in the initial stages of the reaction is slightly different from the gradient in the later stages, which could be an average value and thus affect the graph of the rate of overall crosslinking versus D.C.M.B. concentration, considerably. As a result, a reaction which is first order in the initial stages, which are under investigation, may have an overall order which is less, for example 0.65.

It can be seen in Figure 55 that the average overall rate of crosslinking remains constant during a reaction. However, in the initial stages, the rate of intermolecular crosslinking is greater than the rate of intramolecular crosslinking. As the reaction proceeds, the rate of the intermolecular reaction decreases and the rate of the intramolecular reaction increases. Approaching the gel point, the rate of intermolecular crosslinking is extremely low but the rate of intramolecular crosslinking is increasing rapidly. During a crosslinking reaction, in addition to the size of a molecule increasing, it also tends to be more spherical. The result is that intramolecular crosslinks may be formed between two chains which are already linked by an intermolecular reaction as well as between two sections of an original chain. Thus the probability of intramolecular crosslinking is much higher than that of intermolecular crosslinking in the later stages of the reaction, as observed.

The rate constants which were calculated previously are undoubtedly composite since each reaction, between an aromatic unit in polystyrene and a chloromethyl group in D.C.M.B., is most likely to occur in two steps, namely complex formation between stannic chloride and a chloromethyl group, followed by reaction of the complex with an aromatic nucleus. Since there are two chloromethyl groups in D.C.M.B., the rate constant is composite of four reactions. However, Grassie and Meldrum[16] have shown that the second chloromethyl group is approximately twenty times more reactive than the first and so the rate constants calculated previously may be considered as refering mainly to the slower reaction of the first chloromethyl group, which is the rate determining step.

4.5 Summary.

Reaction mixtures of known concentrations of D.C.M.B., polystyrene and stannic chloride in D.C.E. were allowed to condense for known times, at 30°C. The progress of the reactions were followed by HCl evolution and the change in molecular weight of the initial polystyrene. The overall concentration of crosslinks, at various reaction times, was determined from the HCl evolution and the corresponding concentrations of intermolecular crosslinks from the increase in molecular weight of the polystyrene. Knowing these concentrations, the concentration of intramolecular crosslinks, after each reaction period, was determined by difference.

By plotting the concentration of crosslinks against reaction time, the rate of crosslink formation was found for each series of concentrations of reactants. From the rates of the overall, intermolecular and intramolecular reactions, the orders of these reactions with respect to the initial concentrations of the reactants have been determined. The rate constants for the overall, intermolecular and intramolecular reactions were then evaluated.

CHAPTER FIVE.

INVESTIGATIONS INTO MODEL SYSTEMS.

5.1 Introduction.

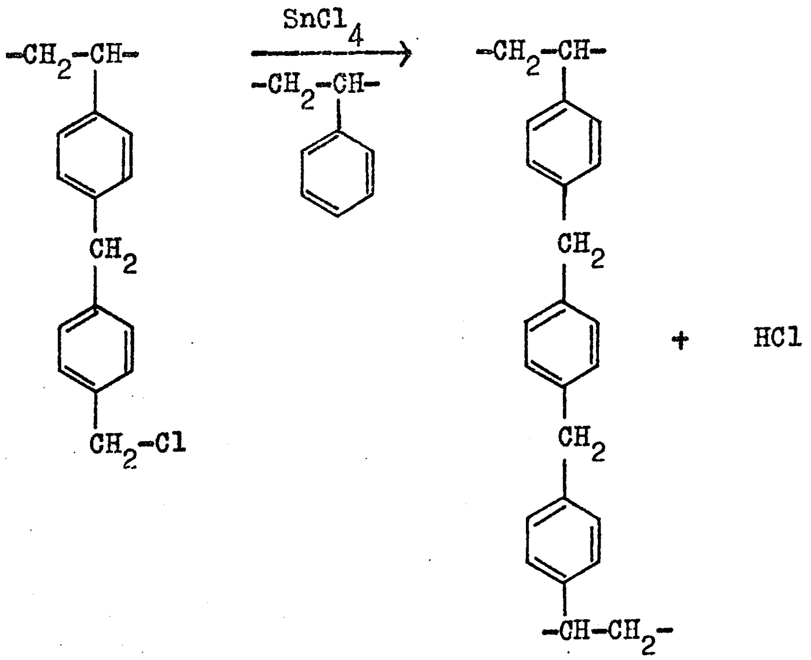
The rate constants which have been determined for the polystyrene/D.C.M.B. condensation are composite since they apply to the reaction of a D.C.M.B. molecule which has two reactive sites. As there is no method by which the rate constants for the reaction of each chloromethyl group in D.C.M.B. in the polystyrene/D.C.M.B. system can be determined independently, an estimate of their values may be obtained by studying model systems.

The reaction between polystyrene and p-methyl benzyl chloride (M.B.C.) may be regarded as a model for the reaction of the second chloromethyl group in D.C.M.B. with polystyrene. Therefore, by studying the kinetics of the polystyrene/M.B.C. condensation, information about the rate constant for the second step in the polystyrene crosslinking reaction should be available, and hence deductions could be made about the value of the rate constant for the first step of the reaction.

The second model system is the condensation between toluene and D.C.M.B. In the benzene/D.C.M.B. condensation[16] and the diphenyl methane/D.C.M.B. condensation,[19] the rate of the reaction of the second chloromethyl group was much faster than that of the first chloromethyl group. Similar results should, therefore, be obtained for the toluene/D.C.M.B. condensation and the polystyrene/D.C.M.B. condensation. Thus, the overall rate constant for the reaction of two aromatic nuclei with one D.C.M.B. molecule should be equivalent to the rate constant for the reaction of the first chloromethyl group, which is the rate determining step. Also, the reaction of two toluene molecules with one D.C.M.B. molecule is equivalent to the formation of one crosslink in the polystyrene/D.C.M.B. system and so comparison of the rate constants obtained for the rate determining steps in the toluene/D.C.M.B. and the polystyrene/D.C.M.B. condensations should yield information concerning the steric effects of polymer molecules on this type of reaction.

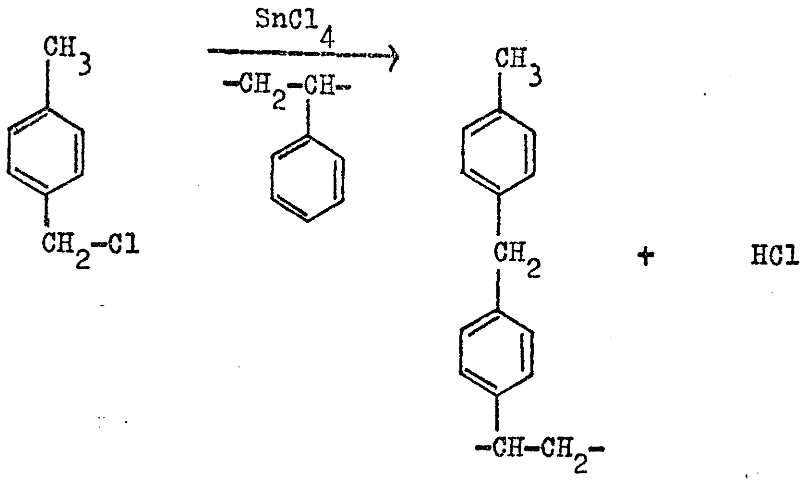
5.2 Polystyrene/M.B.C. Condensation.

The similarity between the reactions involving the second chloromethyl group in D.C.M.B. with polystyrene,



and M.B.C. with polystyrene, shown overleaf, is obvious.

Reaction mixtures of known concentrations of polystyrene, M.B.C. and stannic chloride in D.C.E. were prepared and allowed to react for



various times at 30°C, using the procedures described in Chapter 2. Termination of the reactions was induced by the addition of distilled water and the progress of a reaction followed by titration of the HCl evolved against standard alkali. This method was employed, in preference to the ultra-violet spectroscopy method, since the polymers were not required and so there was no need for isolation and purification.

The concentrations of the reactants are given in Table 10 and the graphs of the concentration of HCl evolved versus reaction time are shown in Figure 56, from the results presented in Table 11. Series 21 contains no polystyrene. Figure 57 shows the above results plotted as a percentage of the total possible yield of HCl. These graphs show that almost complete self-condensation of M.B.C. has occurred in both cases and very little reaction with polystyrene has occurred. Since the percentage of HCl evolved in the series of reactions with polystyrene present is less than that with no polystyrene present, it appears that polystyrene inhibits the self-condensation of M.B.C. The results also show that this self-condensation reaction occurs very quickly and that after a certain percentage condensation, no further reaction occurs.

It is obvious, therefore, that in the reactant concentration range studied, which is comparable to those used in Chapter 4 for the

Table 10.

Concentrations of Reactants in the Polystyrene/M.B.C. Condensations.

Series	(M.B.C.) (mole/l.)	(Polystyrene) (mole/l.)	($SnCl_4$) (mole/l.)
21	0.368	-	0.0045
22	0.368	0.961	0.0045

Table 11.

Relationship between HCl Evolution and Reaction Time.

Series	Time	(HCl) Evolved	
	(hours)	(mole/l.)	% Theoretical
21	24	0.32	85.5
21	48	0.28	75.7
21	72	0.32	85.5
21	96	0.29	78.4
22	24	0.25	67.5
22	48	0.21	56.8
22	72	0.26	70.3
22	96	0.24	65.0

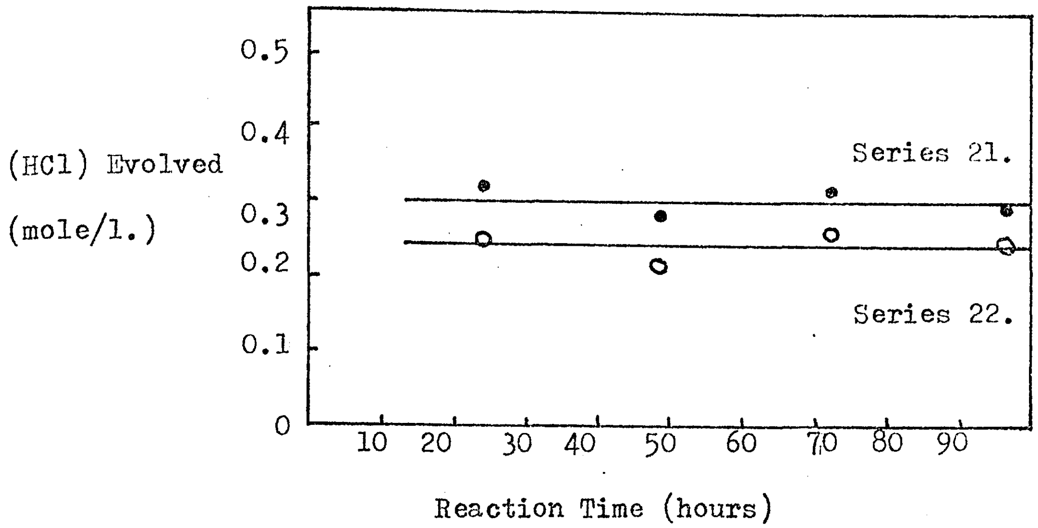


Figure 56. Relationship between HCl Evolution and Reaction Time.

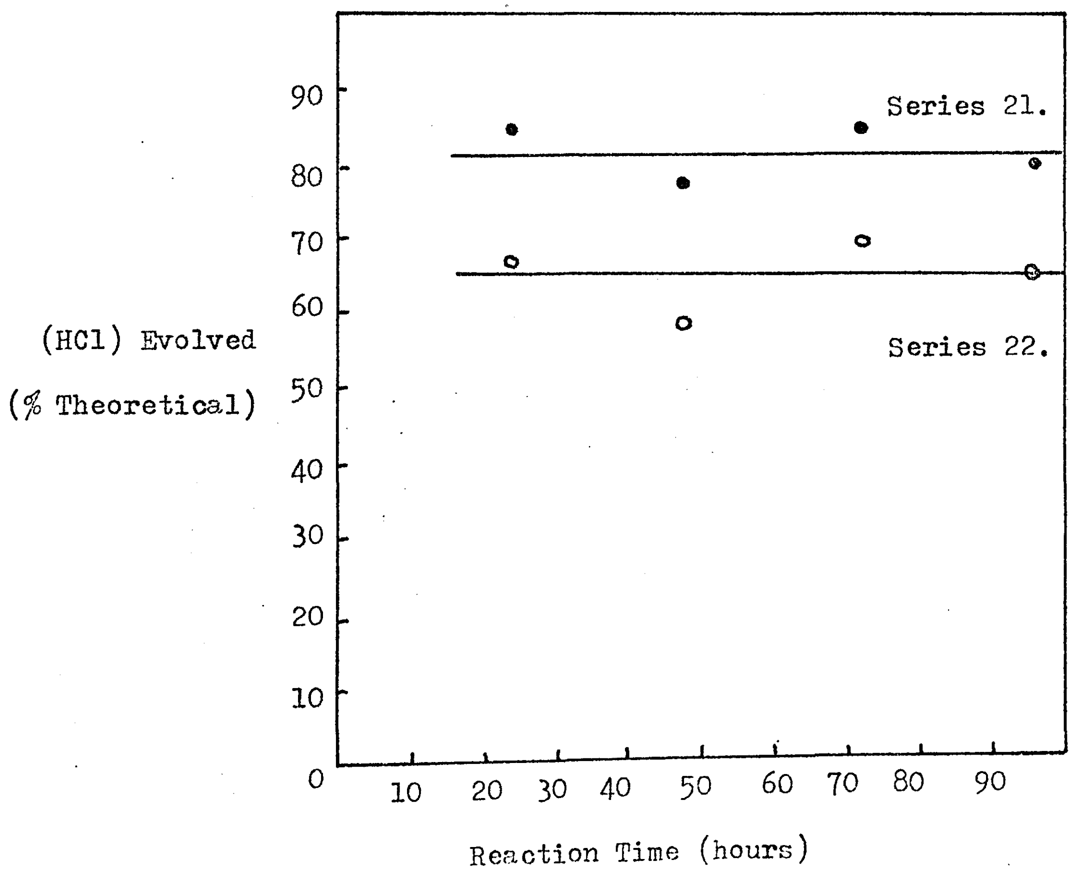


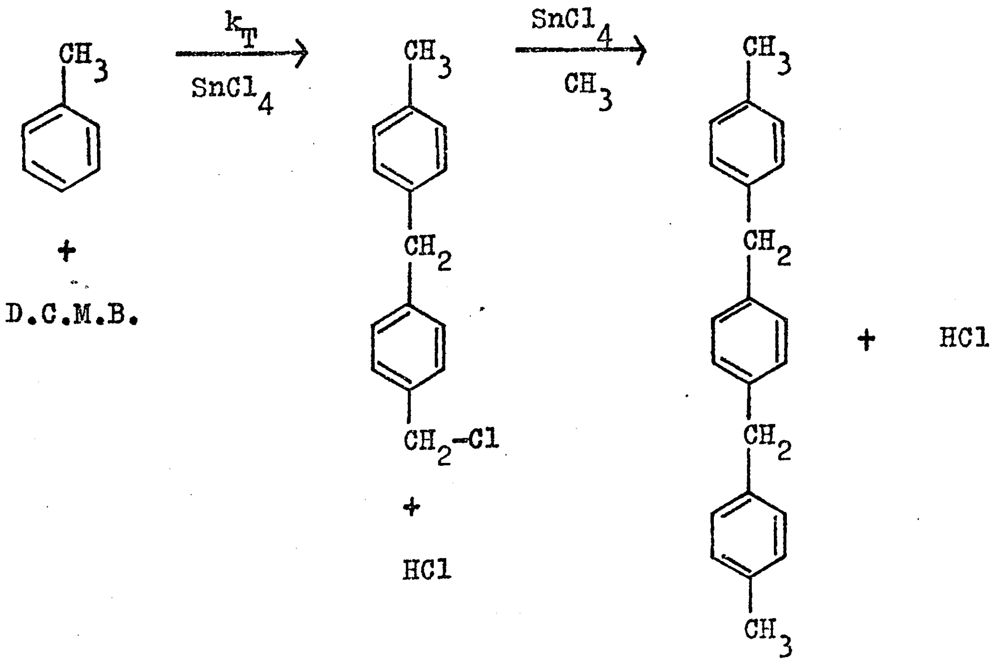
Figure 57. Relationship between Percentage of the Total Possible HCl Evolution and Reaction Time.

polystyrene/D.C.M.B. system, self-condensation of M.B.C. is the predominant reaction and so no useful information could be obtained by studying this system further.

Difficulty had been encountered during the distillation of M.B.C., due to its high vapour pressure, and so the apparent incomplete self-condensation of the M.B.C. might have been due to incomplete transfer of the M.B.C. to the reaction vessel.

5.3 Toluene/D.C.M.B. Condensation.

It has been shown that the early stages of these condensation reactions can be investigated by studying the reaction at conversions of less than 15 %.[16,24] As the purpose of this investigation is the comparison of the reaction of one D.C.M.B. molecule with two aromatic nuclei in polystyrene, with the reaction between toluene and D.C.M.B., it is necessary to limit the reaction to no more than the first 15 %, in order to be sure that it is limited to the condensation of one D.C.M.B. molecule with two toluene molecules.



Using the procedure described in Chapter 2, the mixtures of the concentrations of toluene, D.C.M.B. and stannic chloride in D.C.E. shown in Table 12 were allowed to react at 30°C for various times. The reactions were terminated by the introduction of distilled water and the extent of the reaction was estimated by titration of the HCl evolved with standard alkali. Determination of the degree of reaction by the ultra-violet spectroscopy method was not accurate as a mixture of products was obtained. After titration the products were extracted with D.C.E. as described in Chapter 2.

Typical plots of the variation in the concentration of HCl evolved with reaction time are shown in Figure 58, and all the results are listed in Table 13. These results were obtained after subtracting the value of the titre obtained at zero time. As these plots are linear, the constant rate of HCl evolution, which is a measure of the constant reaction rate, may be determined by calculating the gradients of these curves. In the condensation between polystyrene and D.C.M.B., the reaction was followed by measuring the rate of crosslink formation and since the reaction of the first chloromethyl group in D.C.M.B. is the rate determining step,[16,19,22,24] the rate of crosslink formation is equal to half the rate of HCl evolution. As comparison between the polystyrene/D.C.M.B. condensation and the toluene/D.C.M.B. condensation is desired, it would be more advantageous to follow the toluene/D.C.M.B. system in terms of the formation of p-dixylyl benzene (D.X.B.), than in terms of HCl evolution. Assuming that the reaction of the first chloromethyl group in D.C.M.B. is the rate determining step, then the rate of formation of D.X.B. may be obtained by halfing the rate of HCl evolution. The values obtained for the rate of HCl evolution and the rate of D.X.B. formation are presented in Table 14.

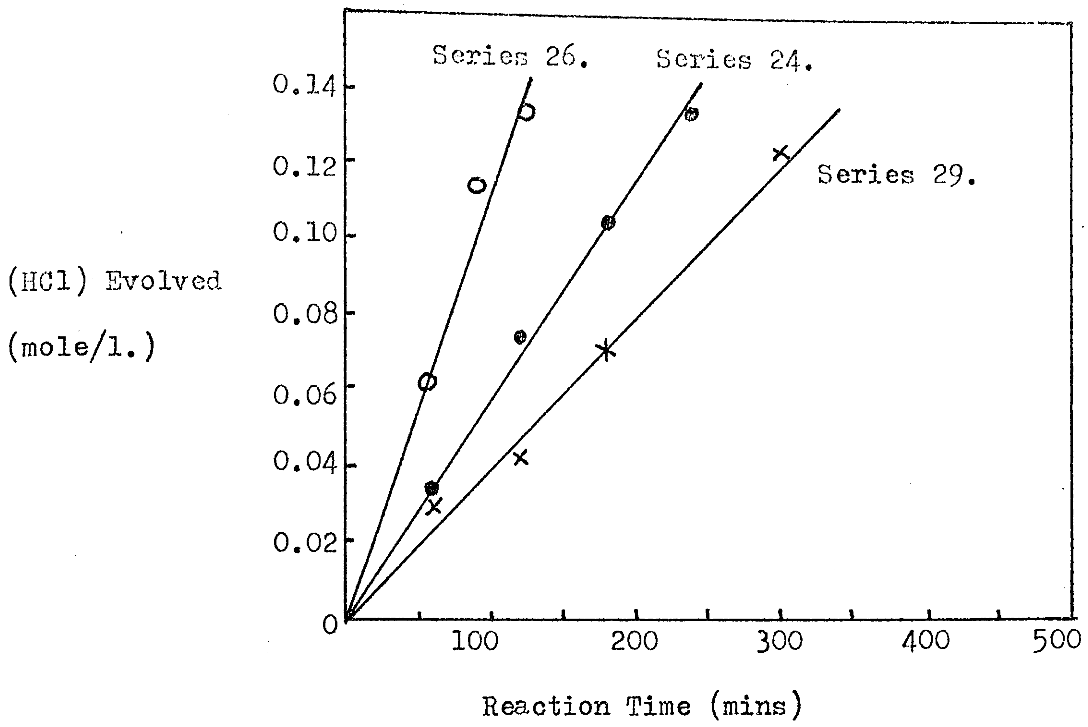


Figure 58. Relationship between HCl Evolution and Reaction Time.

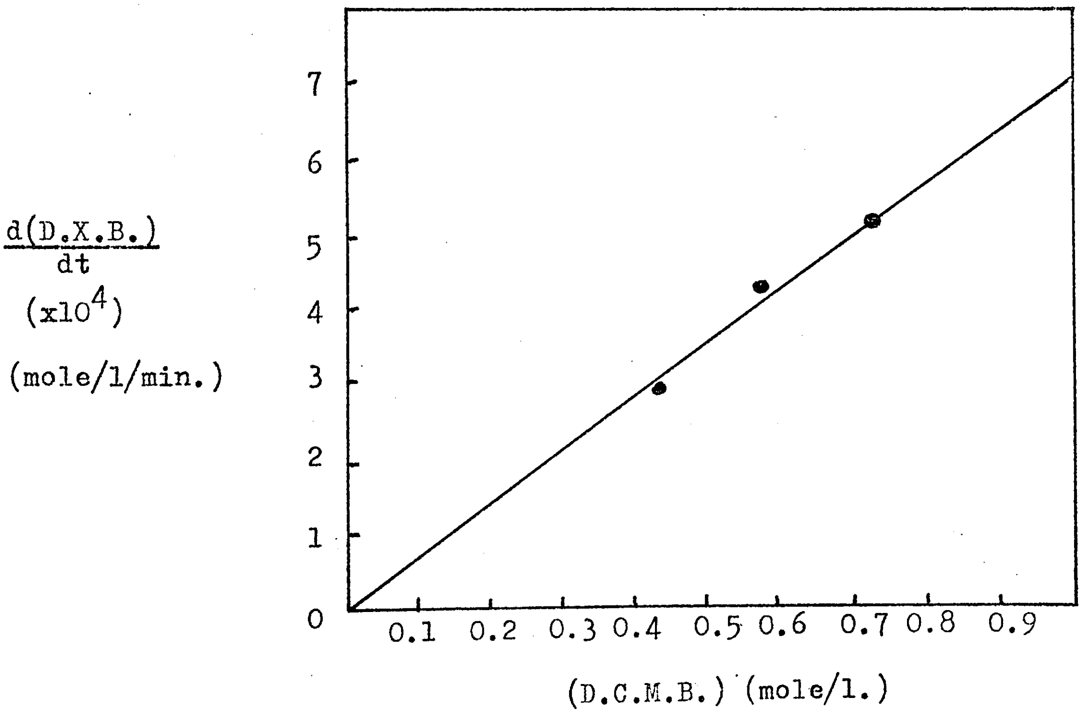


Figure 59. Dependence of Reaction Rate upon Initial D.C.M.B. Concentration.

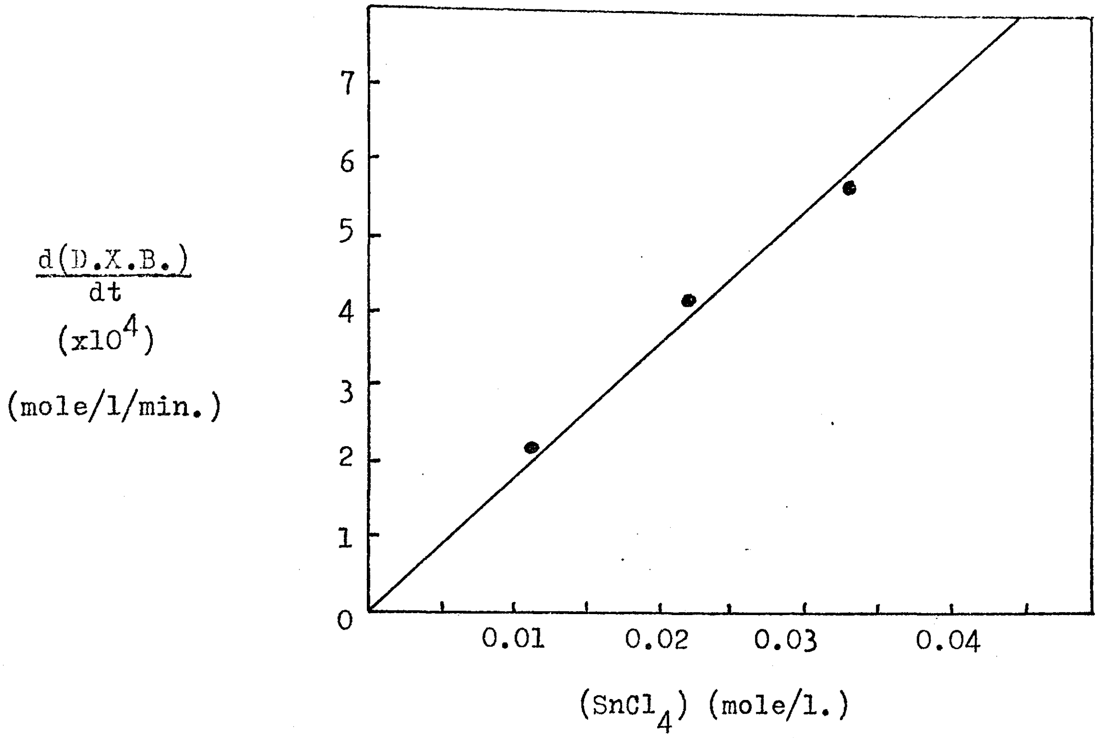


Figure 60. Dependence of Reaction Rate upon Initial Stannic Chloride Concentration.

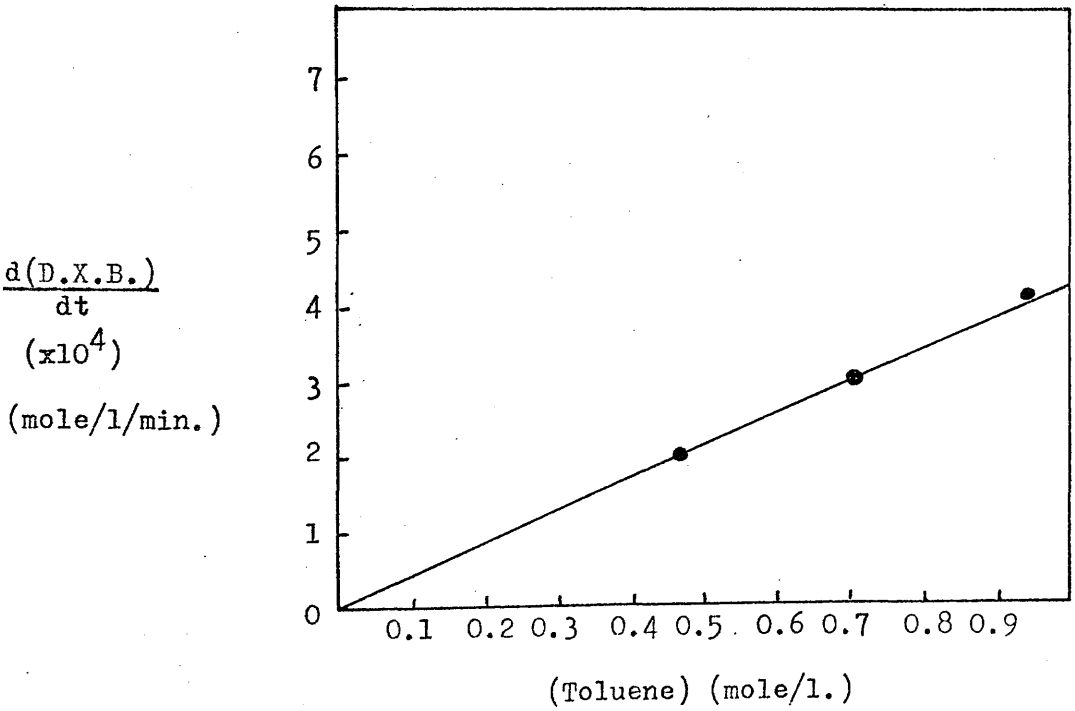


Figure 61. Dependence of Reaction Rate upon Initial Toluene Concentration.

Table 12.

Concentrations of Reactants in the Toluene/D.C.M.B. Condensations.

Series	(D.C.M.B.) (mole/l.)	(Toluene) (mole/l.)	$(SnCl_4)$ (mole/l.)
23	0.572	0.940	0.0217
24	0.429	0.940	0.0217
25	0.715	0.940	0.0217
26	0.572	0.940	0.0326
28	0.572	0.705	0.0217
29	0.572	0.470	0.0217
30	0.572	0.940	0.0109

Table 13.

Relationship between HCl Evolution and Reaction Time.

Series	Time (mins)	(HCl) Evolved (mole/l.)
23	60	0.071
23	120	0.092
23	240	0.214
24	60	0.035
24	120	0.076
24	180	0.104
24	240	0.135

Table 13. (contd.)

Series	Time (mins)	(HCl) Evolved (mole/l.)
25	60	0.062
25	90	0.105
25	120	0.126
25	150	0.150
25	180	0.185
26	60	0.068
26	90	0.118
26	120	0.134
26	180	0.190
28	60	0.037
28	90	0.055
28	150	0.085
28	210	0.134
29	60	0.031
29	120	0.042
29	180	0.070
29	300	0.126
30	60	0.036
30	120	0.054
30	150	0.057
30	240	0.107

Table 14.

Dependence of Rate of Reaction upon Initial Concentrations of Reactants.

Series	(D.C.M.B.) (mole/l.)	$\frac{d(HCl)}{dt}$ (x10^4) (mole/l/min)	$\frac{d(D.X.B.)}{dt}$ (x10^4) (mole/l/min)
23	0.572	8.87	4.44
24	0.429	5.80	2.90
25	0.715	10.27	5.14
	($SnCl_4$) (mole/l.)		
23	0.0217	8.87	4.44
26	0.0326	11.10	5.55
30	0.0109	4.45	2.23
	(Toluene) (mole/l.)		
23	0.940	8.87	4.44
28	0.705	6.00	3.00
29	0.470	4.05	2.03

The relationship between the rate of the reaction and the concentration of each reactant was determined by varying the concentration of each reactant in turn, while maintaining the other two constant. Figures 59, 60 and 61 show the variation of the reaction rate with the initial concentrations of D.C.M.B., stannic chloride and toluene, respectively. The linearity observed illustrates first order dependence in each case.[95]

Thus, the overall rate equation for the early stages of the reaction may be represented by,

$$\frac{d(\text{D.X.B.})}{dt} = k_T(\text{D.C.M.B.})(\text{Toluene})(\text{SnCl}_4)$$

From the large volume of data collected, the average value of the rate constant (k_T) at 30°C has been calculated as,

$$k_T = 4.00 \times 10^{-4}\ \text{l}^2\text{.mole.}^{-2}\text{s.}^{-1}$$

As explained in Chapter 4, this rate constant is probably composite due to complex formation between stannic chloride and each chloromethyl group in D.C.M.B. and the reaction of each complex with toluene.

5.4 Conclusions.

As the rate constant determined for the reaction of two toluene molecules with one D.C.M.B. molecule can be assumed equivalent to the rate constant for the reaction of the first chloromethyl group in D.C.M.B. with one toluene molecule, since this is the rate determining step, comparisons can be made between the rates of the reaction of D.C.M.B. with various aromatic nuclei, at 30°C using stannic chloride as the catalyst in D.C.E. solution, as shown below.

Reactant	Rate Constant	Reference
Benzene	1.10×10^{-4} l.^{2}mole.$^{-2}$s.$^{-1}$	16
Diphenyl methane	5.32×10^{-4} l.^{2}mole.$^{-2}$s.$^{-1}$	19
Benzyl chloride	1.50×10^{-4} l.^{2}mole.$^{-2}$s.$^{-1}$	22
Toluene	4.00×10^{-4} l.^{2}mole.$^{-2}$s.$^{-1}$	-
Polystyrene	1.50×10^{-5} l.mole.$^{-1}$s.$^{-1}$	-

If the benzene/D.C.M.B. condensation is taken as the standard, then due to the activating nature of the methyl group in toluene, an increase in reactivity would be expected in the toluene/D.C.M.B. condensation. Similarly, as the benzyl group in diphenyl methane is more activating than the methyl group in toluene, even higher reactivity would be expected in the diphenyl methane/D.C.M.B. condensation. Also, benzyl chloride should be more reactive than benzene but less reactive than toluene. These predictions agree with the observed results tabulated above.

Polystyrene, however, is much less reactive than these primary aromatic nuclei and so the activating nature of the alkyl backbone in polystyrene must be completely dominated by the steric effects of the large molecules and also the coiling properties unique to polymer molecules. This is predictable since it is difficult for a polymer molecule to arrange itself in the correct conformation for reaction and diffusion of smaller molecules into polymer molecules can also be difficult. The results shown above indicate that although toluene is approximately four times more reactive than benzene, polystyrene is approximately thirty times less reactive than toluene.

5.5 Summary.

The overall rate equation for the crosslinking of polystyrene with D.C.M.B. really describes the first step in the crosslinking process, which is the slow rate determining step. An attempt was made to isolate the fast second step by studying the reaction between polystyrene and M.B.C. Self-condensation of M.B.C. was so fast, however, that this approach had to be abandoned. Using the techniques described in Chapter 4, the kinetic data for the toluene/D.C.M.B. condensation were obtained and the rate constant for the early stages of the reaction evaluated. The reactivity of toluene was compared with the reactivity of polystyrene and other aromatic nuclei.

CHAPTER SIX.

THERMAL ANALYSIS OF CROSSLINKED POLYSTYRENE.

6.1 Introduction.

In this chapter, the effect of the degree of crosslinking on the glass transition temperature (T_g) of polystyrene and on the temperature at which thermal degradation of polystyrene commences, will be investigated and the results discussed with reference to the structure of the crosslinked polystyrene.

6.2 Glass Transition Temperature Measurements.

a) Introduction.

Many methods are available for measuring the T_g of a polymer, especially the standard dilatometric method of Bekkedahl,[98] in which changes in specific volume are measured as a function of temperature, or the commonly used simple cantilever softening point test,[99] which gives an adequate measure of T_g for commercial purposes. However, these methods cannot be used for small quantities or for polymers of very high or low molecular weight which are difficult to mould. More recently, a method[100] has been developed for relatively low molecular weight polymers in which peak width is measured as a function of temperature in the N.M.R. spectra of the polymers. In this investigation, the T_g is measured solely by D.T.A. and D.S.C., since these methods are convenient and accurate.

As no measurable exothermic or endothermic process occurs at the T_g, D.T.A. and D.S.C. must detect a change in heat capacity. The interpretation of thermograms has been discussed in detail[86] for D.T.A. but not much literature is at present available on the more modern D.S.C. methods.

Various workers[101-103] have employed different techniques for the interpretation of D.T.A. thermograms but as the technique applied by Keavney and Eberlin[101] involved measuring the temperature at the sample centre, which is the method employed in the Du Pont 900 Thermal Analyzer, their treatment has been applied to the thermograms obtained in this investigation. As glass transitions involve no latent heat changes but do involve specific heat changes, only a shift in the baseline occurs in these thermograms, and since this effect is very small, high sensitivity is required. Keavney and Eberlin said that the T_g occurs at the intersection of the lines formed before and after the change in the ΔT versus T curve. Although they found that T_g was independent of heating rate, a sharper 'break' in the curve occurs with higher heating rates.

Discrepancies and anomalous results are evident in the literature concerning transition temperature measurements, but these can all be explained[104] by the polymer history and instrument design and sensitivity, as different results may be obtained on samples of the same composition but in different morphological states. The results reported here are regarded as being accurate with respect to each other, although they may differ slightly from previous investigations. This precision was obtained by using identical conditions for each determination and by ensuring that each polymer sample was subjected to identical pre-treatment.

Glass transitions are similar[105,106] to second order transitions in which a change in secondary thermodynamic properties occurs without a change in latent heat. Below the T_g, sufficient thermal energy exists in the polymer only to allow the atoms to vibrate about an equilibrium position and so the polymer is glassy and brittle. Above the T_g, segmental motion occurs, the polymer then exhibiting tough, flexible and rubbery properties.

Boyer and Spencer[107] studied the effect of molecular weight on the T_g of polystyrene and found that in the molecular weight range 1,500 to 60,000, there is a linear relationship between T_g and molecular weight but between 60,000 and 300,000, the T_g remains constant.

It has been shown that T_g measured by D.S.C. is dependent upon heating rate[107] and pre-treatment[109,110] but as long as these are identical for a series of samples, meaningful comparisons can be made. In this investigation it was found that D.S.C. was much more accurate and reproducible than D.T.A., mainly due to the 'noise' in the baseline of the D.T.A. which accompanies the high sensitivity required. Information regarding the enthalpy of the transition was also obtained by D.S.C. Typical D.T.A. and D.S.C. thermograms are shown in Figures 62 and 63, respectively.

As in the case of D.T.A., past investigators have used various points on the D.S.C. thermogram to define the T_g. For consistency with D.T.A. the T_g was obtained by the method described earlier for D.T.A. but the endothermic peak minimum (T_{min}) was also recorded for comparison with other investigations. The result of these investigations was that the relationship between the degree of crosslinking and the T_g was determined.

b) Differential Thermal Analysis.

As D.T.A. has been superceeded by D.S.C. for the purpose of this investigation, the results will only be presented here and discussed

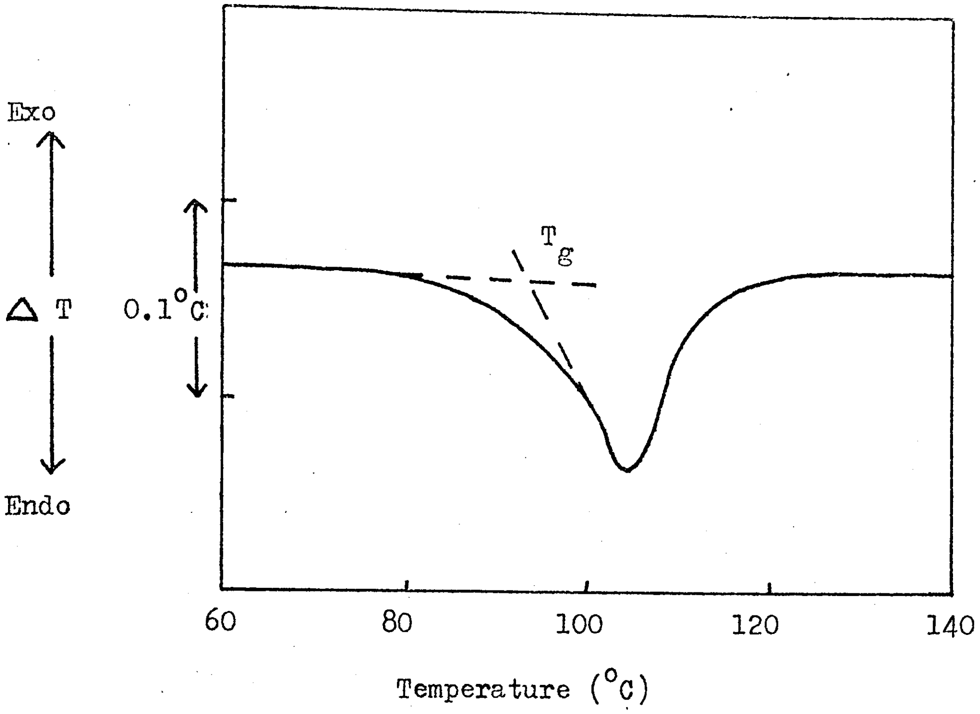


Figure 62. D.T.A. Thermogram of Polystyrene. ($\overline{M}_n$ - 13,500)

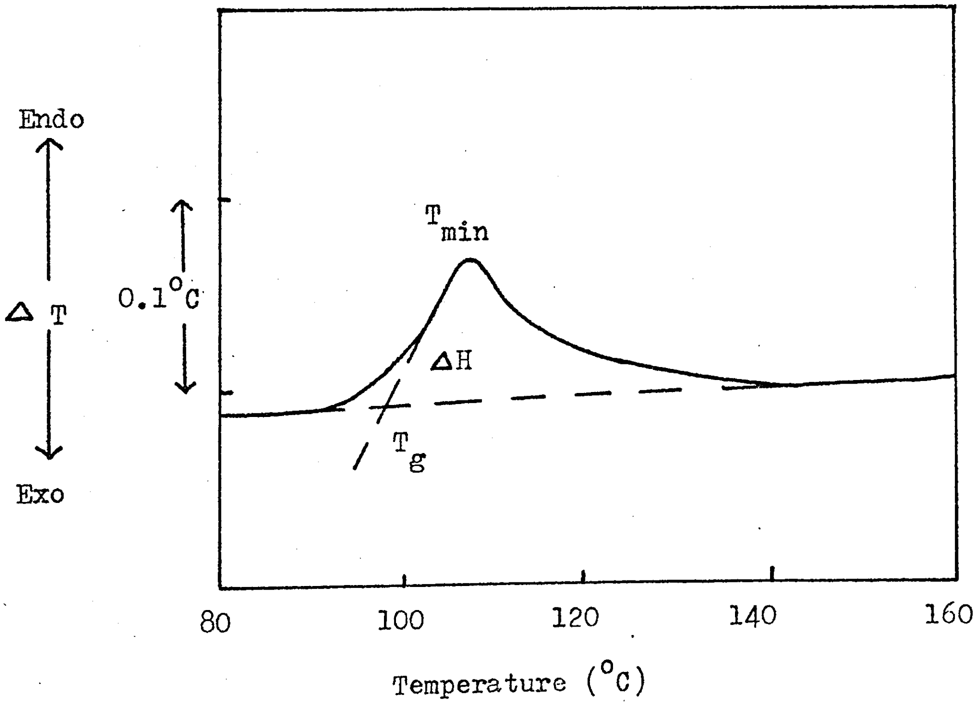
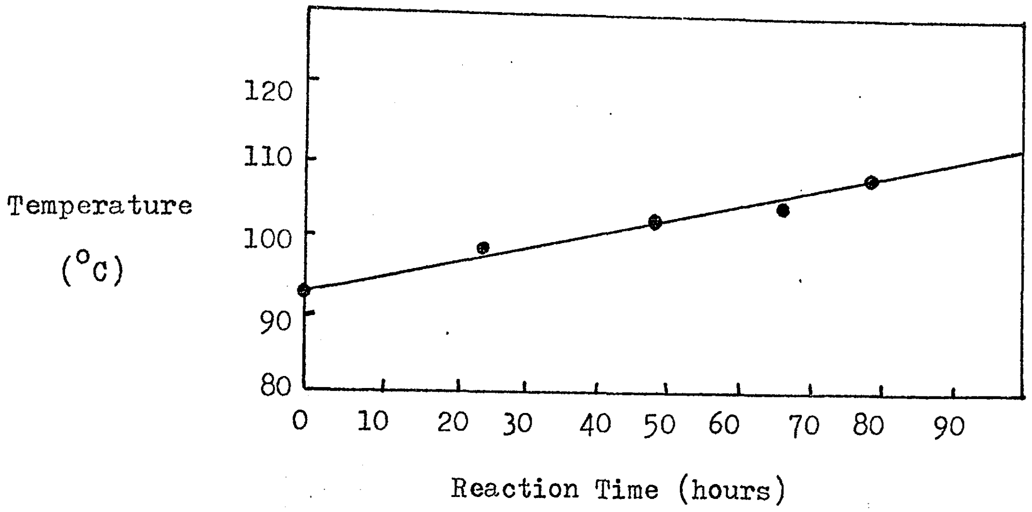
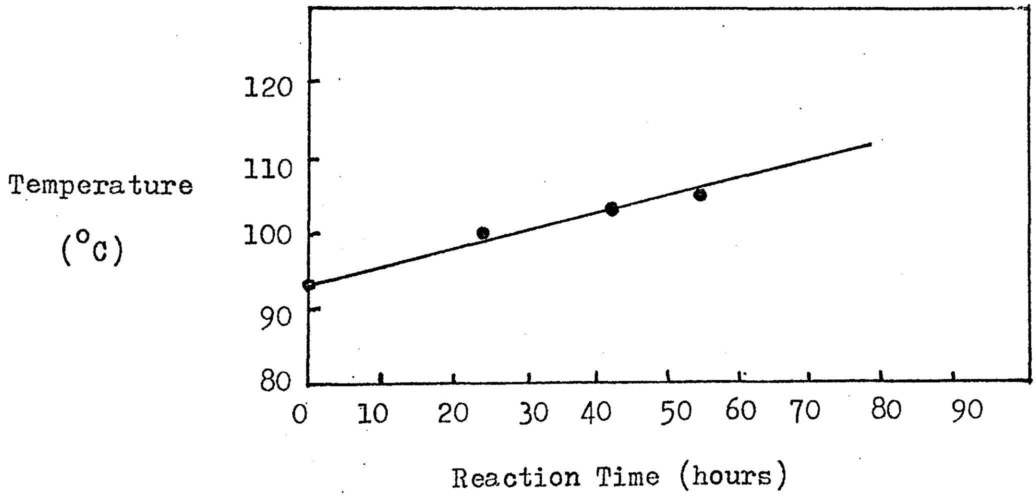


Figure 63. D.S.C. Thermogram of Polystyrene. ($\overline{M}_n$ - 13,500)



(a) Series 10.



(b) Series 12.

Figure 64. Relationship between Degree of Crosslinking and Glass Transition Temperature measured by D.T.A.

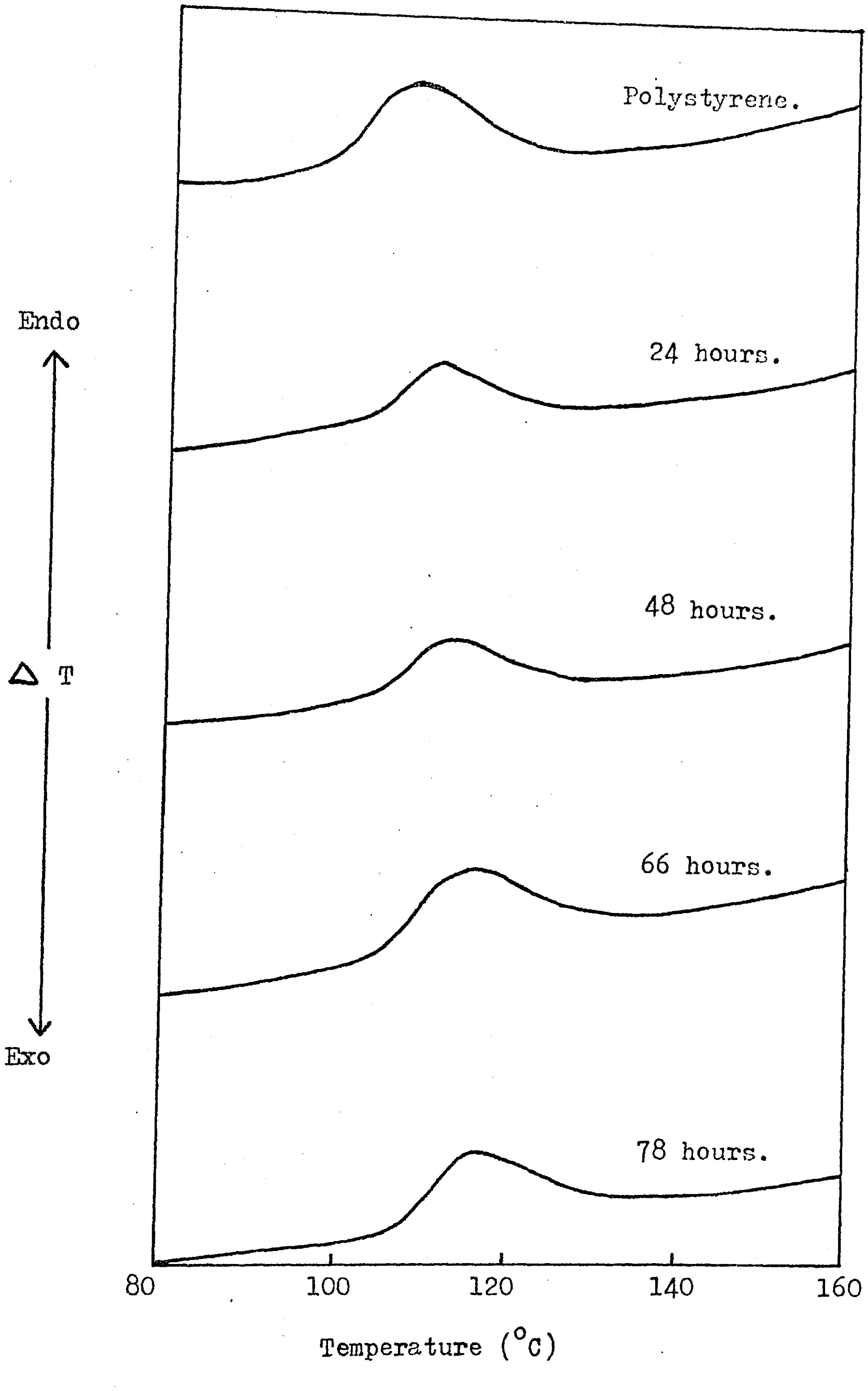


Figure 65. Five Typical D.S.C. Thermograms showing an Increase in Crosslinking Reaction Time Shifting the Endotherms to Higher Temperatures. (Series 10.)

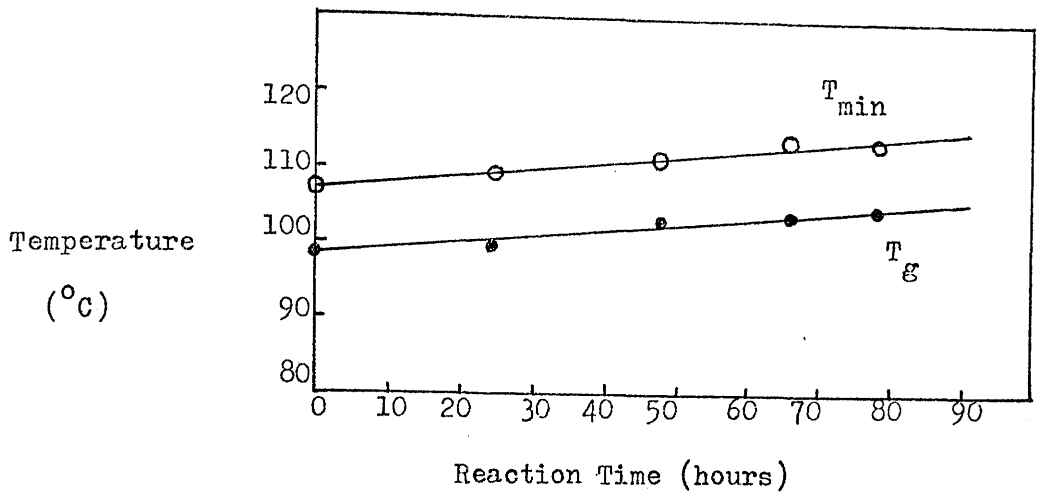


Figure 66. Relationship between Degree of Crosslinking and Glass Transition Temperature measured by D.S.C. (Series 10.)

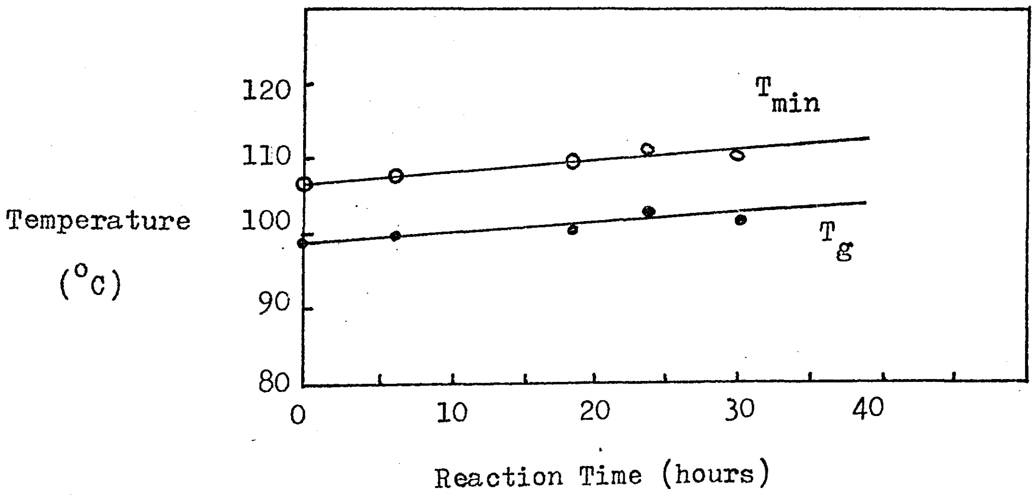


Figure 67. Relationship between Degree of Crosslinking and Glass Transition Temperature measured by D.S.C. (Series 17.)

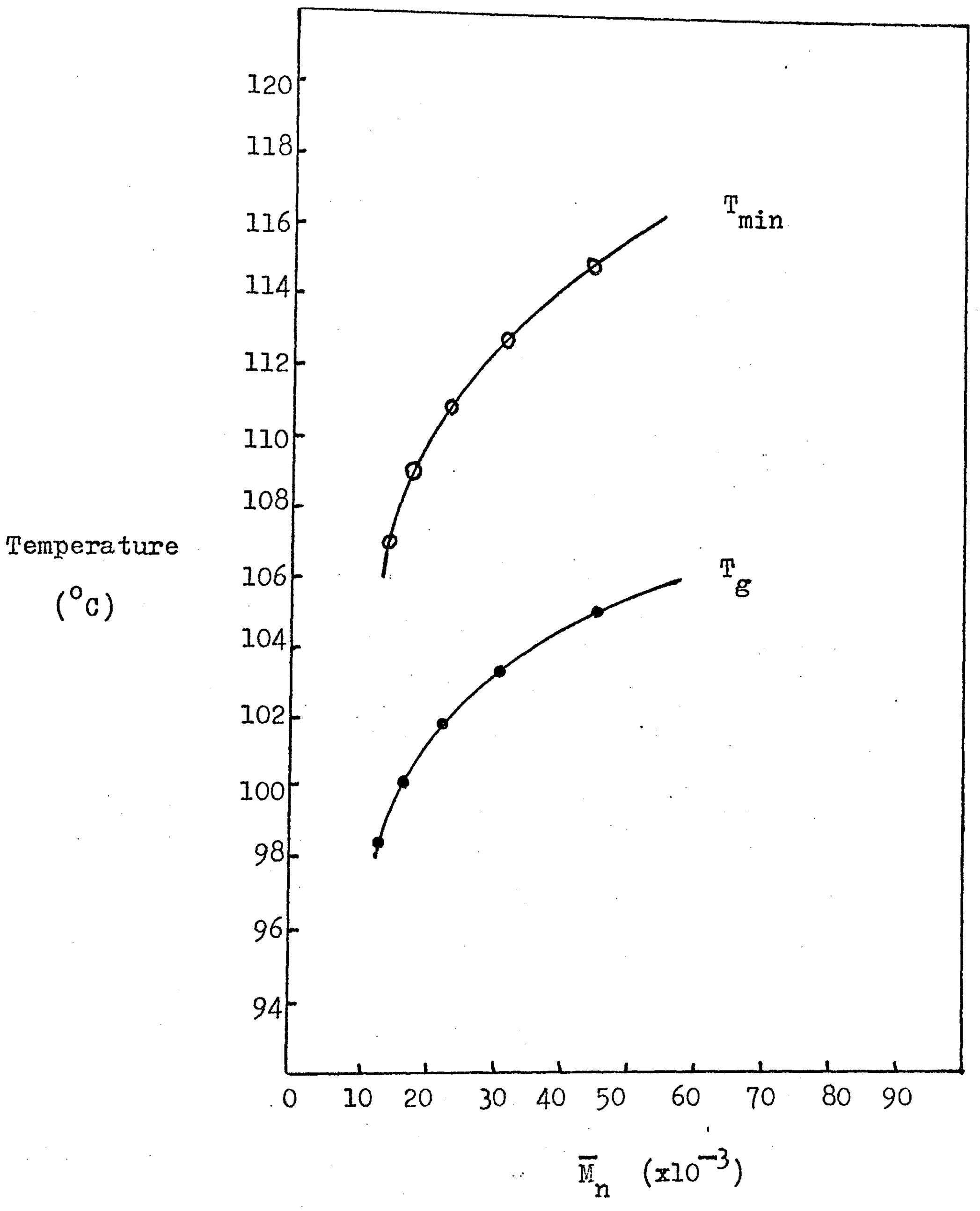


Figure 68. Relationship between Glass Transition Temperature measured by D.S.C. and Molecular Weight. (Series 10.)

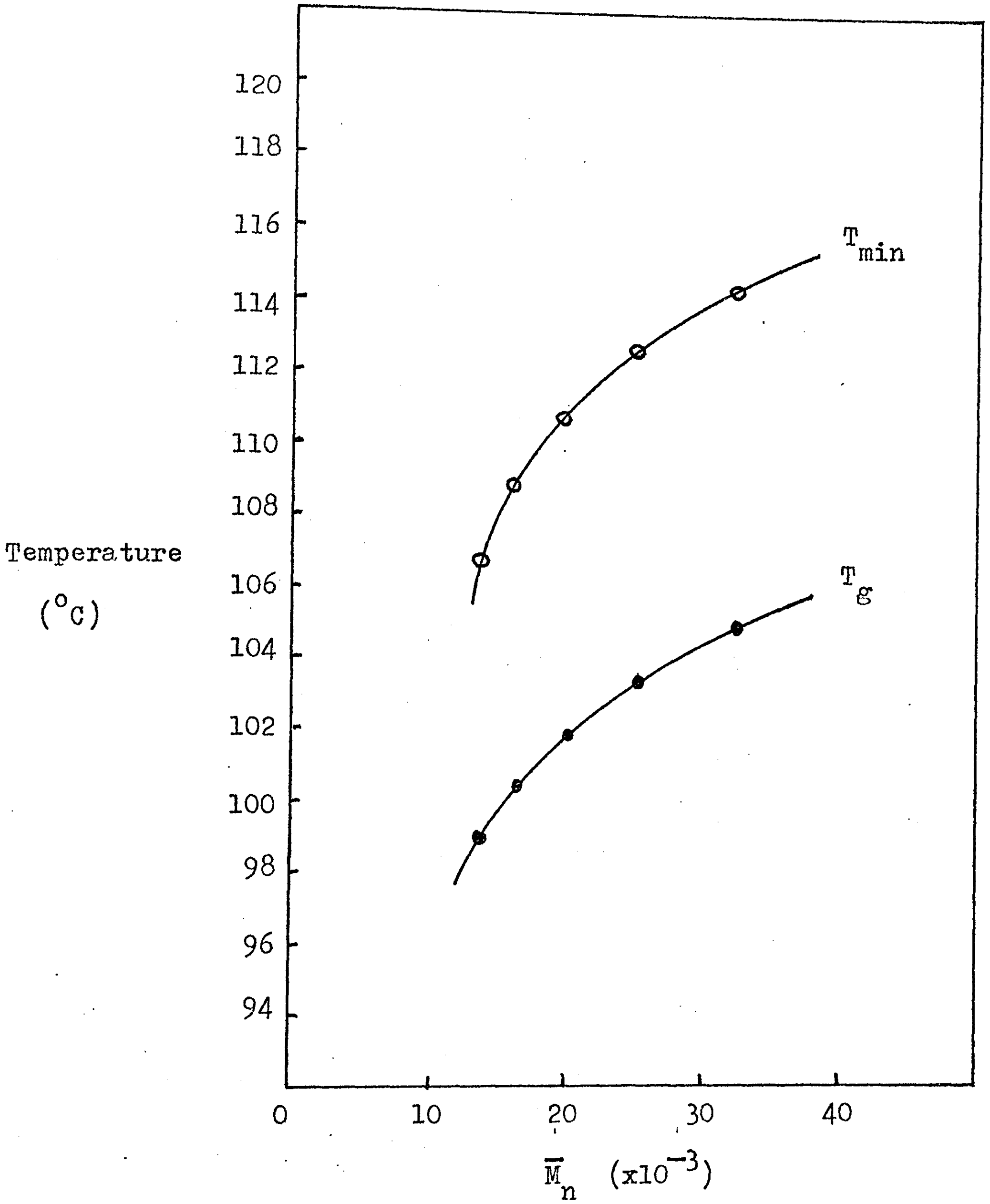


Figure 69. Relationship between Molecular Weight and Glass Transition Temperature measured by D.S.C. (Series 19.)

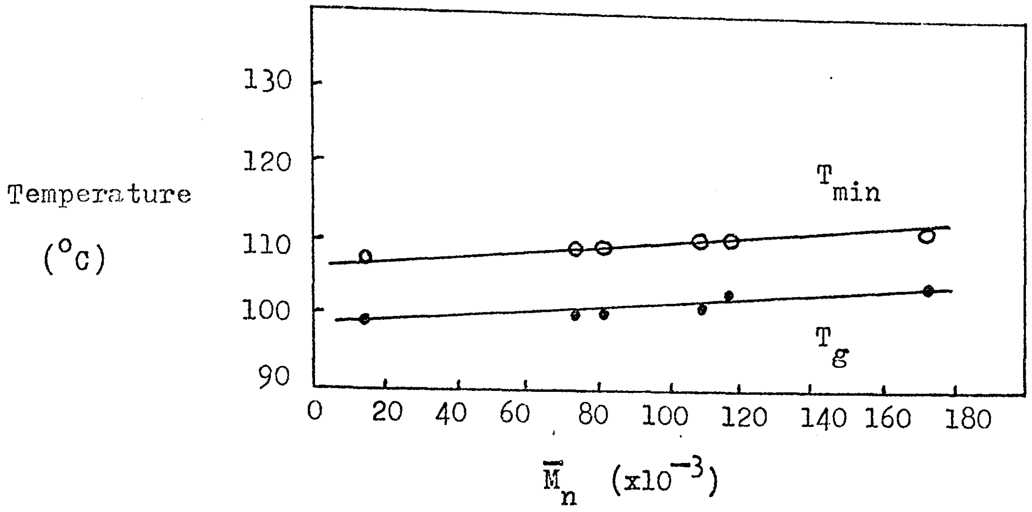


Figure 70. Relationship between Glass Transition Temperature and Molecular Weight for Linear Polystyrene.

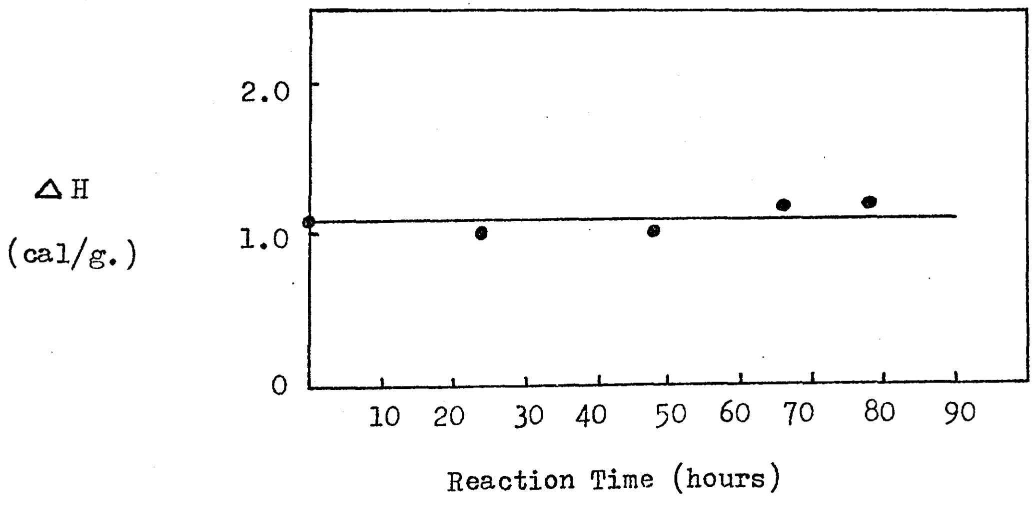


Figure 71. Relationship between Heat of Transition and Degree of Crosslinking. (Series 10.)

Table 15.

Relationship between Degree of Crosslinking and Glass Transition Temperature measured by D.T.A.

Series	Reaction Time (hours)	T_g (°C)
Polystyrene	-	93
10	24	100
10	48	103
10	66	104
10	78	107
11	24	103
11	42	101
11	54	105
12	24	101
12	42	103
12	54	105

Table 16.

Relationship between Degree of Crosslinking and Glass Transition Temperature measured by D.S.C.

Series	Time (hours)	T_g (^oC)	T_{min} (^oC)	ΔH (cal/g.)
Polystyrene	-	99	107	1.10
10	24	100	109	0.97
10	48	103	111	0.98
10	66	104	114	1.17
10	78	105	114	1.16
11	24	104	110	0.94
11	42	105	112	0.86
11	54	105	114	0.89
12	24	103	108	1.06
12	42	103	110	0.88
12	54	105	113	0.94
13	30	101	109	0.79
13	66	105	112	0.81
13	100	105	114	1.06
15	72	106	116	0.90
15	114	108	120	1.10
15	144	112	126	0.89

Table 16. (contd.)

Series	Time (hours)	T_g (^{o}C)	T_{min} (^{o}C)	ΔH (cal/g.)
16	24	97	108	0.96
16	54	104	112	0.94
16	78	105	114	1.12
16	96	108	117	0.91
17	6	100	108	0.93
17	18	100	109	1.32
17	24	103	111	1.06
17	30	101	110	0.98
18	18	101	110	1.09
18	24	101	111	1.03
18	27	103	113	0.99
19	6	101	108	1.16
19	18	105	114	0.80
19	20	105	115	1.02

Table 17.

Relationship between Glass Transition Temperature and Molecular Weight for Crosslinked Polystyrenes.

Series	Time (hours)	$\overline{M}_n$ ($\times 10^{-4}$)	T_g ($^\circ C$)	T_{min} ($^\circ C$)
Polystyrene	-	1.35	99	107
10	20	1.55	100.5	109
10	40	2.25	102	111
10	60	3.10	103.5	113
10	80	4.40	105	115
11	20	1.90	102	109.5
11	40	2.80	104.5	112
11	50	3.50	106	113.5
11	60	4.50	107.5	114.5
12	20	1.80	101.5	109
12	40	2.60	104	111
12	50	3.20	105	112
12	60	4.00	106.5	113
13	40	1.55	102	110
13	70	2.00	104.5	112
13	90	2.60	106	114
13	110	3.70	108	116

Table 17. (contd.)

Series	Time (hours)	$\overline{M}_n$ ($\times 10^{-4}$)	T_g ($^\circ$C)	T_{min} ($^\circ$C)
15	50	1.90	103.5	113
15	90	2.75	107	118
15	120	3.80	110	122
15	150	5.60	113	127
16	30	1.90	101.5	110
16	60	2.85	104	113
16	80	3.90	106	115
16	100	5.70	108	117
17	10	1.70	100	108
17	20	2.10	101	109
17	30	2.70	102	110.5
17	40	3.80	103.5	111.5
18	10	1.80	100	109
18	20	2.40	101	111
18	25	2.90	102	112
18	30	3.60	103	113
19	5	1.60	100.5	109
19	10	2.00	102	110.5
19	15	2.50	103.5	113
19	20	3.20	105	114.5

Table 18.

Relationship between Glass Transition Temperature and Molecular Weight for Linear Polystyrenes.

$\overline{M}_n$	T_g(°C)	T_{min}(°C)	Method of Preparation	
13,500	99	107	Cationic	30°C
72,700	100	109	Radical	100°C
80,800	100	109	Radical	100°C
108,000	101	110	Cationic	78°C
116,000	102	110	Thermal	140°C
171,000	104	111	Radical	60°C

Table 19.

Relationship between Glass Transition Temperature and Number of Crosslinks per gram of Polystyrene.

Series	$\frac{\Delta T_g}{\beta}$ (x10^{-4})
10	4.3
11	4.8
12	3.2
13	6.4
15	4.7
16	4.0
17	3.0
18	1.9
19	3.6

later with those obtained by D.S.C. Two typical graphs of T_g versus reaction time are presented in Figure 64 and all the results obtained, which showed similar trends, are listed in Table 15.

c) Differential Scanning Calorimetry.

Figure 65 shows five D.S.C. traces, the uppermost being for polystyrene itself and the other four for polystyrene with increasing degrees of crosslinking. It is instantly obvious that the position of the endotherm moves to a higher temperature as the degree of crosslinking increases. As stated earlier, the T_g was taken as being the temperature at which the intersection of the lines formed before and after the change in the slope of the curve occurs. Also, T_{min}, the temperature at which the endothermic peak minimum occurs was also recorded. These temperatures were plotted against the time of crosslinking, which is a measure of the degree of crosslinking and the curves obtained are shown in Figure 66, the upper line and lower line resulting from the T_{min} and T_g values, respectively. It is apparent that a linear relationship exists over the degree of reaction studied, (up to the gel point). All the series of reactions showed identical trends, the results being tabulated in Table 16 and another typical series being shown in Figure 67. These results are obviously similar to those obtained by D.T.A. and presented in Figure 64.

It has been shown in Chapter 4 that the number average molecular weight increases with reaction time and typical plots of T_{min} and T_g versus $\overline{M}_n$ are presented in Figures 68 and 69. These two figures are typical of all the series investigated, the data for which are recorded in Table 17.

These results demonstrate that over the range of crosslinking studied, the T_g increased by approximately 9^oC. This may be due either to a molecular weight effect[107] or to crosslinking. To clarify this, T_g measurements were made on the series of polystyrenes of varying molecular weight, listed in Table 18, the values obtained being plotted in Figure 70. It can be seen that the T_g does increase linearly with the $\bar{M}_n$, but over the range studied in this thesis, which is up to a molecular weight of 60,000, an increase of only 1°C occurs. This indicates that while a small increase in the T_g may occur with an increase in molecular weight, the major effect is due to crosslinking. It is reasonable to expect that more energy is required for segmental motion as the degree of crosslinking increases.

Figures 66 and 67 demonstrate that the T_g increases linearly with the degree of crosslinking for each series of reactions. Similar results were obtained by Fox and Loshaek[111] for copolymers of styrene and divinyl benzene in which the following empirical relationship was found to apply,

$$\Delta T_g = \sim 7 \times 10^4 \beta$$

where ΔT_g is the increase in T_g due to a certain degree of crosslinking and β is the number of moles of crosslinks per gram of polymer.

By calculating $\Delta T_g/\beta$ for each series of reactions and recording the results in Table 19, it was found that for polystyrene crosslinked by D.C.M.B., a similar relationship holds, namely,

$$\Delta T_g = \sim 4 \times 10^4 \beta$$

From the area under the peaks on the D.S.C. traces, the enthalpy of the transition was calculated as described in Chapter 2. It was found that, within the accuracy of the measurements, the heat of the transition is independent of the degree of crosslinking or the molecular weight of polystyrene. A typical plot of the enthalpy of the transition (ΔH) versus reaction time is shown in Figure 71 and all the results collected are presented in Table 16. A mean value of 1.0 cal/g. was obtained and this agrees with the values of 0.92 cal/g. calculated by Lambert[109] and 1.0 cal/g. determined by Merrill and Gibbs.[112]

6.3 Thermal Stability Investigations.

Although there is still much conjecture about the thermal degradation mechanism for polystyrene, it was considered outwith the scope of this thesis to pursue this further. The results presented here merely show the effect of the degree of crosslinking on the thermal stability of polystyrene. For this purpose, T.V.A. and T.G.A. were the two techniques employed.

a) Thermal Volatilisation Analysis.

50mg. powder samples were heated to 500°C at a linearly programmed heating rate of 10°C/min., using the D.C.T.V.A. apparatus.[88] The chain fragments, collected as the cold ring fraction above the reaction vessel were always colourless and no residue remained at 500°C. Volatile products collected were all gaseous under vacuum at room temperature. Figure 72 shows typical T.V.A. traces for (a) polystyrene, (b) poly(p-methyl styrene) and (c) crosslinked polystyrene, respectively. In these curves, several features are significant, namely, the temperature at which volatilisation commences (T_v), the temperature at which the rate of volatilisation reaches a maximum (T_{max}) and the shape of the traces.

Polystyrene itself shows a T_{max} at about 426°C and a T_v at about

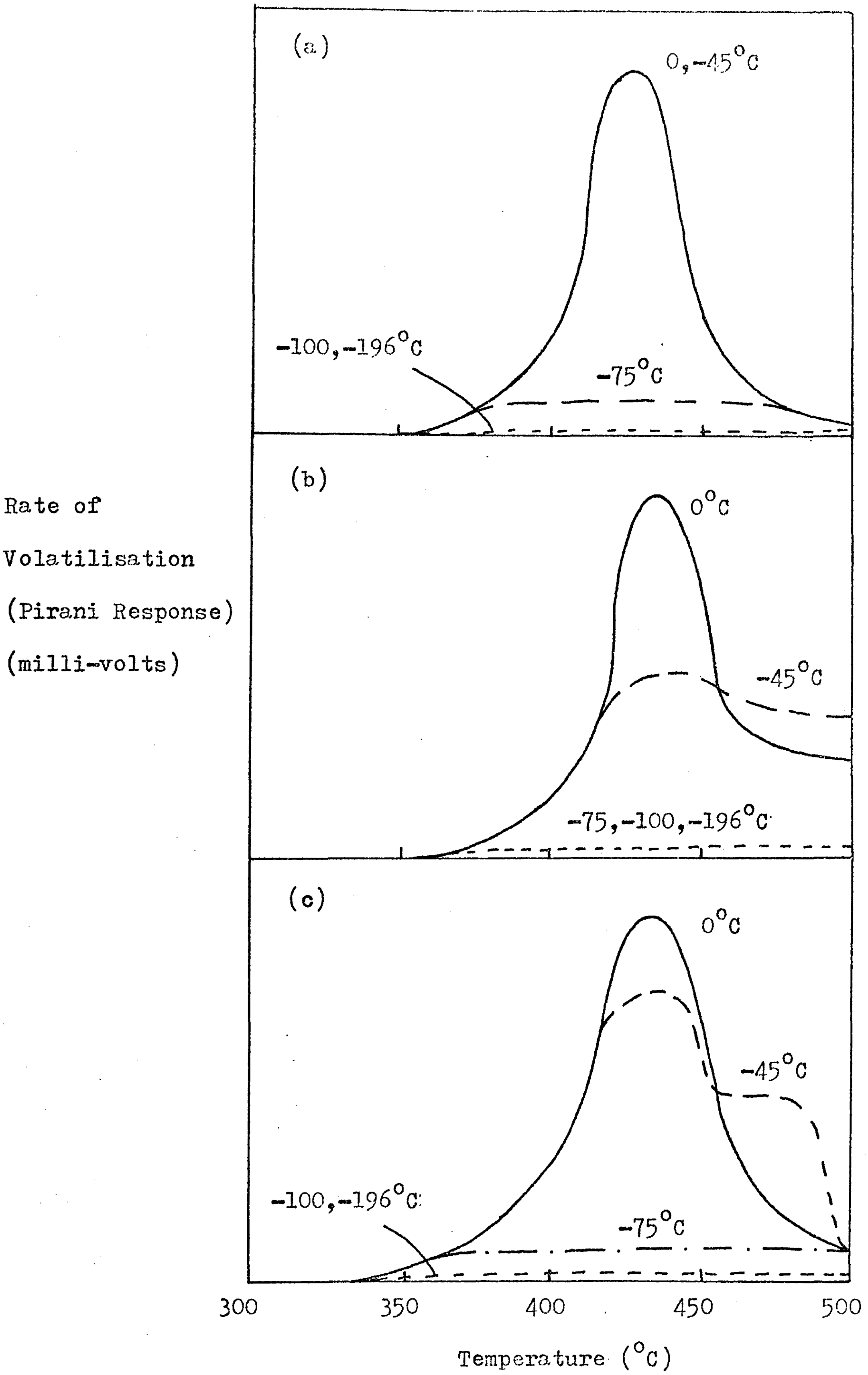


Figure 72. D.C.T.V.A. Thermograms of (a) Polystyrene (b) Poly(p-methyl styrene) and (c) Polystyrene Crosslinked for 66 hours (Series 10.).

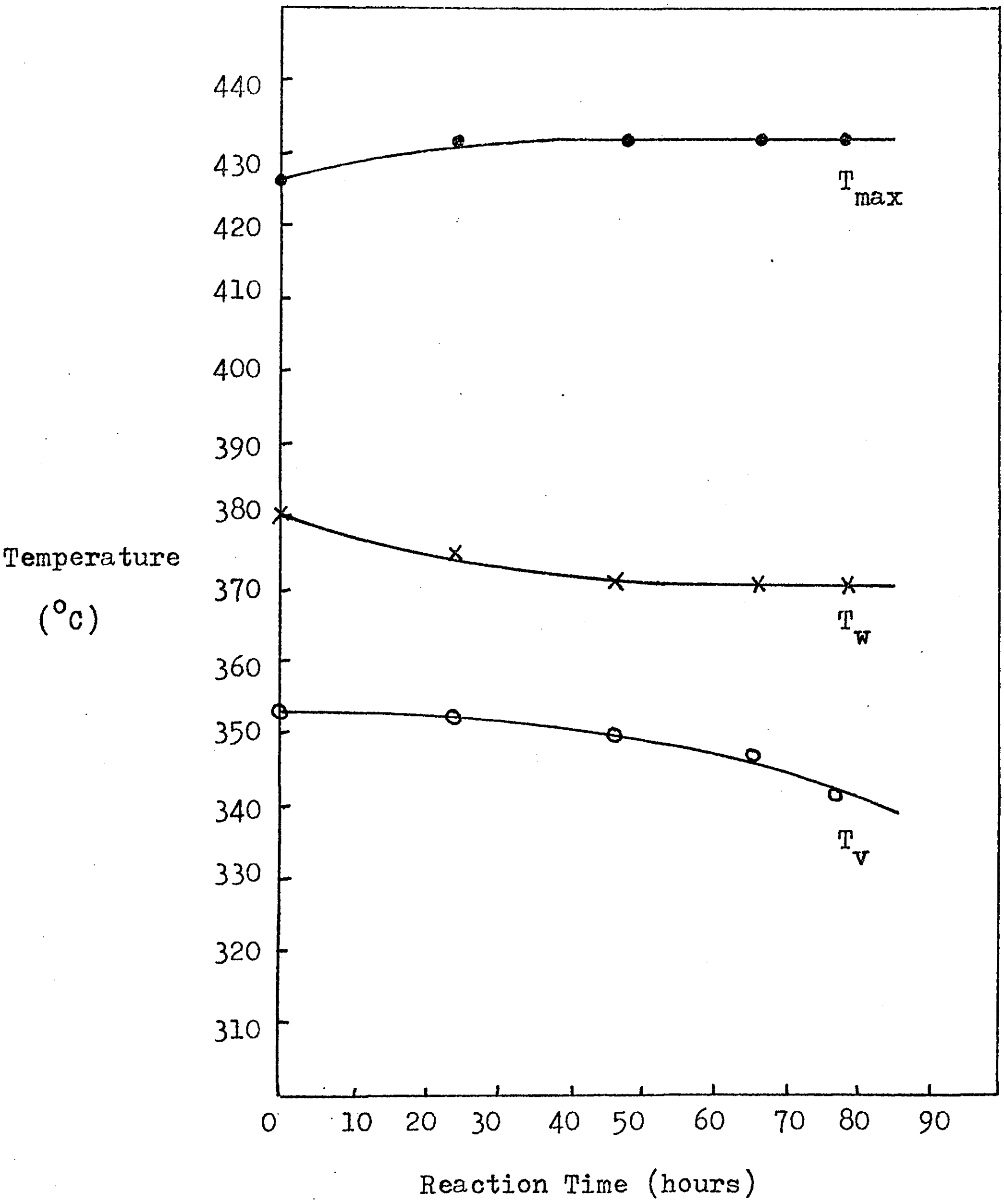


Figure 73. Relationship between Degradation Temperature and Degree of Crosslinking. (Series 10.)

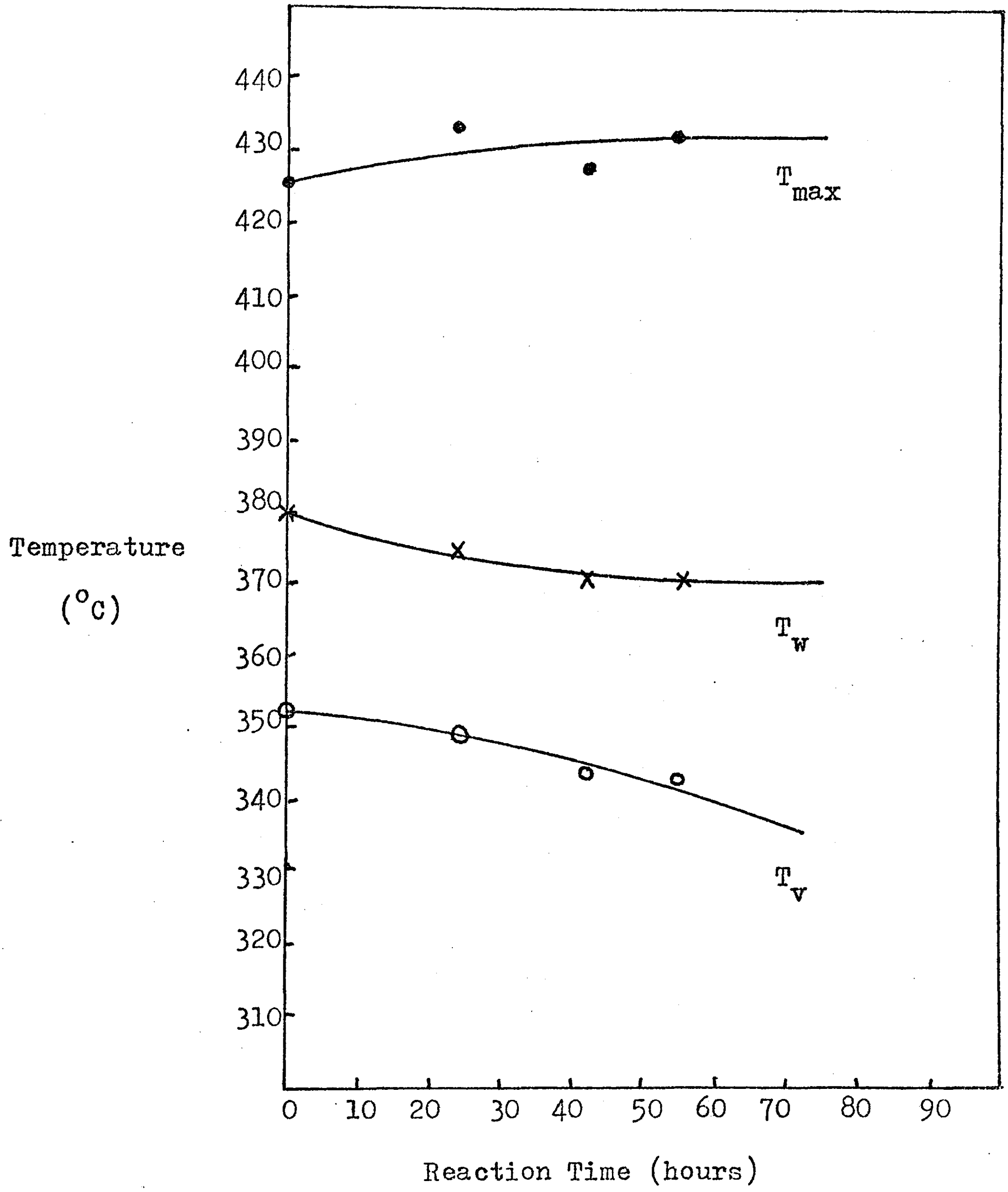


Figure 74. Relationship between Degradation Temperature and Degree of Crosslinking. (Series 11.)

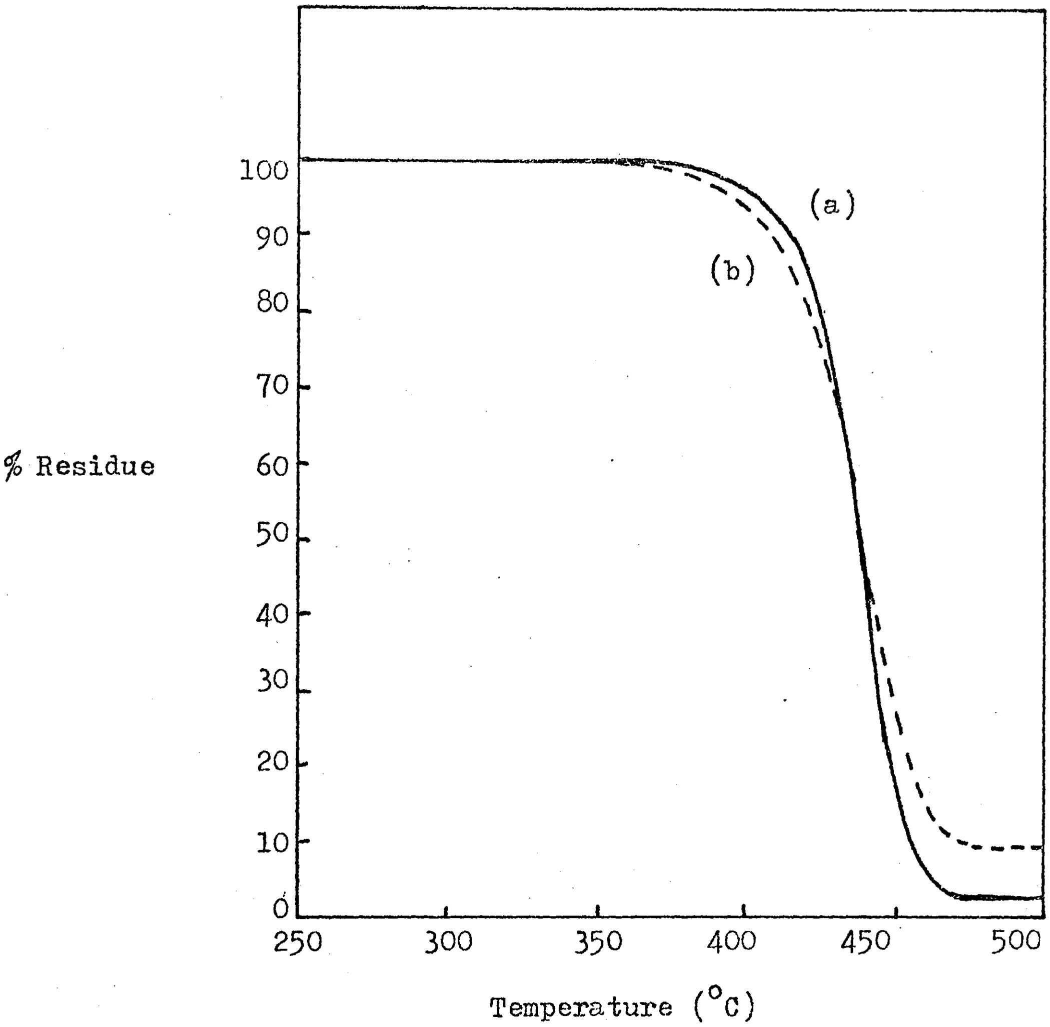


Figure 75. T.G.A. Thermograms of (a) Polystyrene and (b) Polystyrene Crosslinked for 78 hours (Series 10.).

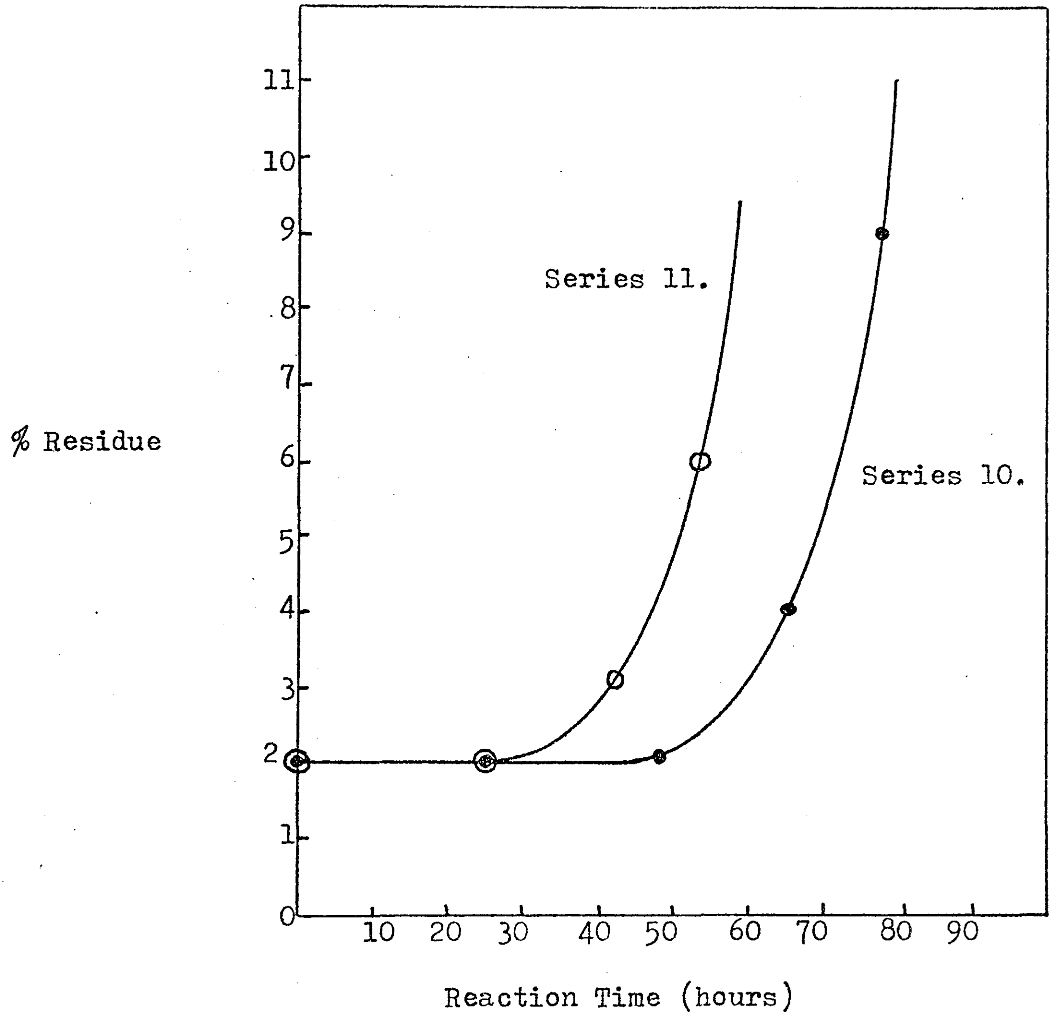


Figure 76. Relationship between Degree of Crosslinking and Percentage Residue at 500°C measured by T.G.A.

Table 20.

Relationship between Degree of Crosslinking and Degradation Temperature measured by D.C.T.V.A.

Series	Reaction Time (hours)	T_v (^oC)	T_{max} (^oC)
Polystyrene	-	353	426
10	24	352	432
10	48	349	432
10	66	337	432
10	78	331	432
11	24	349	435
11	42	343	426
11	54	343	432
12	24	349	435
12	42	343	429
12	54	337	432
13	30	352	435
13	66	349	435
13	100	343	435
14	18	349	432
14	30	346	432
14	44	343	435
14	54	341	432

Table 20. (contd.)

Series	Reaction Time (hours)	T_v (^oC)	T_{max} (^oC)
15	72	352	436
15	114	343	432
15	144	339	432
16	24	352	432
16	54	349	432
16	78	343	432
16	96	337	432

Table 21.

Variation of Degree of Crosslinking with Degradation Temperature and Residue measured by T.G.A.

Series	Reaction Time (hours)	T_W (^oC)	Residue (% Initial)
Polystyrene	-	380	2
10	24	375	2
10	48	370	2
10	66	370	4
10	78	370	9
11	24	375	2
11	42	370	3
11	54	370	5
12	24	375	2
12	42	370	3
12	54	370	6

353°C, as shown in Figure 72(a). The 0°C and -45°C traces are coincident indicating no condensation at -45°C, but the -75°C trace shows a small limiting rate for the distillation of a product from the -75°C trap to the -196°C trap. At -100°C there is complete condensation of the products. Calibration tests[88] with styrene confirm this limiting rate at -75°C and the complete condensation at -100°C. This is consistent with the known degradation behaviour of polystyrene, since with the possible exception of dimer, all the products other than monomer would be expected to collect as the cold ring fraction.

Poly(p-methyl styrene) gives a similar trace to that of polystyrene with both the T_v and T_{max} being approximately 10°C higher. A more notable difference, however, is that a limiting rate occurs at -45°C and condensation is complete at -75°C. This limiting rate at -45°C is presumed to be due to p-methyl styrene monomer.[88]

The T.V.A. thermogram of a crosslinked polystyrene, shown in Figure 72(c) shows the T_v at 337°C which is approximately 15°C lower than for polystyrene and the T_{max} at 432°C, which is about 5°C higher than for polystyrene. This means that the temperature at which degradation commences is lower in crosslinked polystyrene than in linear polystyrene, yet the temperature at which the maximum rate of volatilisation occurs, is higher.

The lower degradation temperature must, therefore, be related to the presence of crosslinks and similar results have been observed for branched poly(vinyl chloride)[113] and polypropylene.[114,115] It has been proposed that branch points may be sources of the initiation of degradation, due either to strain in the molecule due to coiling, which applies in this case, or to the presence of tertiary or quaternary carbon atoms. Also, the lowering of the degradation temperature in a branched polymer compared with the corresponding linear polymer appears to be related to the number and length of the branches, since it has been observed that the rate of the initiation of degradation, at constant temperature, increases with the number and length of the branches.

The higher T_{max} in the crosslinked polystyrene suggests that scission may be occurring in the crosslinks as well as in the polystyrene backbone, since the T_{max} could result from a combination of polystyrene and poly(p-methyl styrene) behaviours. Further evidence that the thermogram represents a mixture of the above two types, is that limiting rates at -45°C and -75°C are both present. This may be due to styrene and units similar to p-methyl styrene, which can only be obtained from partially degraded crosslinks, but this does not explain whether scission occurs first in the backbone or in the crosslinks. T_{max} is probably higher in the crosslinked polystyrene and poly(p-methyl styrene) because of hyperconjugation, due to the p-alkyl residue or the p-methyl group, respectively, which cannot occur in polystyrene. This causes even more stabilisation of the reactive radical formed than in polystyrene itself.

Typical trends in T_v and T_{max} with the degree of crosslinking are shown in Figures 73 and 74 and all the results are presented in Table 20.

The volatile degradation products and chain fragments of polystyrene and the crosslinked polystyrenes were compared by infra-red spectrophotometry using either a gas cell with NaCl windows or a smear between NaCl plates. No differences could be detected, probably since the absolute degree of crosslinking is small even in the relatively highly crosslinked products.

b) Thermogravimetric Analysis.

10mg. samples were heated to 500°C at a linearly programmed heating rate of 10°C/min., under an atmosphere of nitrogen, in the

Du Pont 950 Thermogravimetric Analyzer and Figure 75 shows typical weight loss versus temperature traces for polystyrene and a highly crosslinked polystyrene. It can be seen that the crosslinked polystyrene is approximately 10°C less stable than the linear polystyrene but that a higher percentage residue remains at 500°C.

Two examples of the variation in the degradation onset temperature (T_W) with the degree of crosslinking are shown in Figures 73 and 74 and all the results are listed in Table 21. These show trends comparable to the T_V results, in that the initiation of degradation occurs at a lower temperature in highly crosslinked polystyrene. The difference in the actual values of T_V and T_W is probably due to the different conditions which necessarily exist in the T.V.A. and T.G.A. apparatus.

One point of interest is the increase in the residue at 500°C with an increase in the degree of crosslinking. This implies that residues of the crosslinks must be present under T.G.A. conditions, but no information was obtained as to whether they are complete crosslinks or partially degraded crosslink residues, as suggested by T.V.A. Figure 76 shows typical plots of percentage residue versus the degree of crosslinking, the values being collected in Table 21.

6.4 Summary.

The results presented in this chapter have shown that although the T_g increases with an increasing degree of crosslinking, the temperature at which the onset of thermal degradation occurs, decreases. Since segmental motion is more restricted as the amount of branching increases, the increase in the T_g confirms the expected results since more energy must be supplied to a molecule for vibration to occur. The T.V.A. and T.G.A. thermograms suggest that the presence of crosslinks in polystyrene decreases its thermal stability either by initiating premature scission in the polystyrene backbone or by scission of the crosslinks.

CHAPTER SEVEN.

FRIEDEL-CRAFTS REACTIONS ON STYRENE COPOLYMERS.

7.1 Introduction.

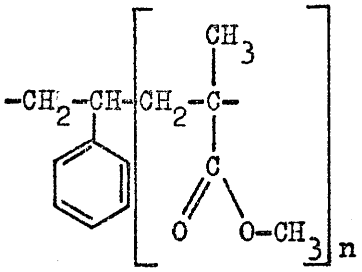
It has been shown in Chapter 4 that in the presence of Friedel-Crafts catalysts, D.C.M.B. may be used to crosslink polystyrene. This method of crosslinking is limited since there are few polymers which contain aromatic nuclei. However, if small percentages of styrene are copolymerised into other polymers, then the aromatic nuclei present in the styrene units should be available as sites at which crosslinking may occur.

7.2 Styrene/Methyl Methacrylate System.

Using the procedures described in Chapter 2, the polymers listed in Table 22 were prepared and purified. The number average molecular weights of the polymers were determined and the initiator concentrations were chosen to produce molecular weights in the region of 10,000 so that considerable amounts of reaction would occur before the onset of gelation. Copolymer compositions were calculated from micro-analytical data. Thus for a copolymer of styrene and methyl methacrylate, having the structure shown overleaf,

$$\% \text{ Oxygen} = \frac{32n}{118 + 100n} \times 100$$

If the percentage of oxygen in the copolymer is determined by elemental analysis, then n is easily calculated using this formula.



A similar procedure was employed for all copolymers used in this study.

a) Copolymers of Methyl Methacrylate and Styrene.

Employing the experimental procedures described in Chapter 2, reaction mixtures were prepared so that the reactant concentrations corresponded to those used in the polystyrene crosslinking reactions. 1g. of D.C.M.B., 2g. of poly(methyl methacrylate-co-styrene) (10/1) and 1 ml. of 0.087 M stannic chloride solution in D.C.E. were made up to 20 ml. with D.C.E., flushed with nitrogen, sealed and allowed to react at 60°C. No colouration was observed after long time intervals and after precipitation, spectroscopic analysis showed that the product was identical with the initial copolymer.

Since no reaction had occurred, the reactant concentrations were increased to 4g. of the copolymer, 1g. of D.C.M.B. and 10 ml. of a 0.87 M stannic chloride solution, made up to 20 ml. with D.C.E. and this mixture was allowed to react at 60°C. The solution which was originally colourless, gradually darkened to a dark brown colour and after five days, gelation occurred forming a dark brown residue. The reaction was repeated and the products precipitated into a 50 % methanol/distilled water mixture before the gel point, to obtain a sample of the crosslinked product. On precipitation of the coloured solution of the

Table 22.

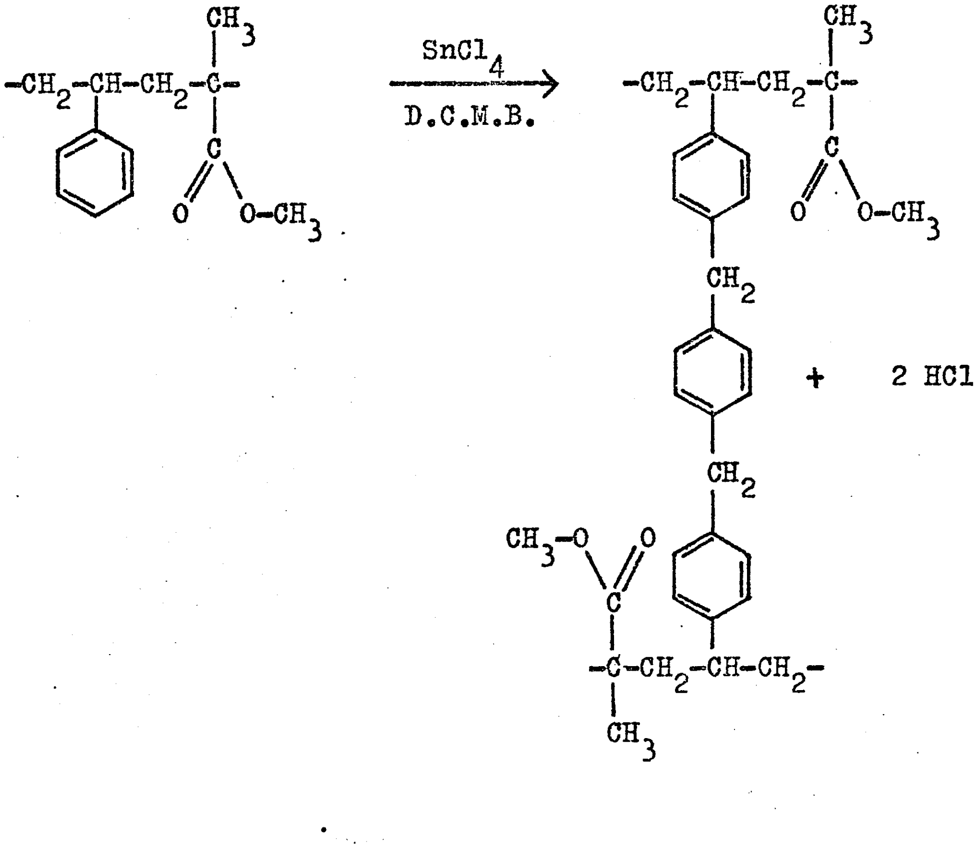
Composition and Molecular Weight of the Styrene/Methyl Methacrylate System Copolymers.

Polymer	Composition	$\overline{M}_n$
Polystyrene	-	13,500
Poly(methyl methacrylate)	-	10,200
Poly(methyl methacrylate-co-styrene)	10/1	5,100
	5/1	6,500
	1/1	6,800
Poly(methyl methacrylate-co-2,6-dimethyl styrene)	5/1	7,800
Poly(methyl methacrylate-co-m-methyl styrene)	12/1	9,600
Poly(methyl methacrylate-co-p-methyl styrene)	10/1	12,000
Poly(methyl methacrylate-co-m-chloro styrene)	10/1	9,000
Poly(methyl methacrylate-co-p-chloro styrene)	10/1	8,100
Poly(methyl methacrylate-co-p-methoxy styrene)	8/1	9,800

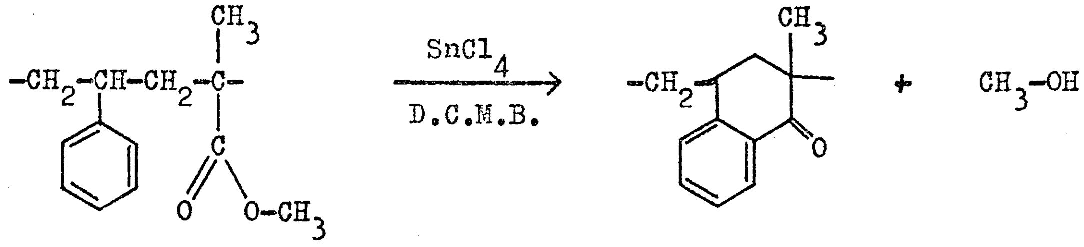
polystyrene reaction mixture used in Chapter 4, the colour disappears leaving a white precipitate but in these reactions the precipitate is dark brown. This suggests that an alternative reaction may be occurring either in addition to the crosslinking reaction or in preference to it.

The reaction was, therefore, repeated using identical quantities of reactants and conditions except that no D.C.M.B. was present. As in the previous reaction, the colourless solution darkened until after five days it was dark brown but still very mobile and gelation only occurred after fourteen days reaction time. Thus, a second reaction must be occurring in competition with crosslinking in the copolymer/D.C.M.B. mixture.

The expected reaction is the Friedel-Crafts alkylation process, which has already been discussed,



However, it seemed possible that a Friedel-Crafts acylation might occur between the ortho position of the aromatic nucleus and the ester portion of the neighbouring methacrylate group,



As gelation occurs more quickly with D.C.M.B. present in the reaction mixture and as HCl is detected after opening the reaction ampoule, it is clear that the two reactions must be occurring simultaneously. Also, gelation occurs in the absence of D.C.M.B. and so the darkening of the product as the reaction proceeds, could be due to the increasing amount of conjugation as more cyclic structures are produced. These experiments were repeated with the 5/1 and 1/1 copolymers and similar trends were observed.

Using the 5/1 copolymer of methyl methacrylate and 2,6-dimethyl styrene but with identical concentrations of the copolymer and the stannic chloride in D.C.E., with and without D.C.M.B. present, reactions were allowed to proceed at $60^{o}C$ under nitrogen. In the reaction mixture containing D.C.M.B., the colourless solution darkened and gelation occurred, to form a black tar, after three days. No signs of reaction or colouration were observed after sixteen days in the reaction mixture with no D.C.M.B. present. The crosslinking reaction, therefore, must be occurring as in polystyrene when D.C.M.B. is present. In absence of D.C.M.B., however, the second reaction is inhibited by the ortho substituents on the aromatic ring. This is in accordance with the occurrence of the acylation reaction at the ortho position on the aromatic nuclei as suggested above. Reaction at the meta and para positions is unlikely due to the strain which would be present in the product.

Using the KBr disc technique, infra-red spectra were obtained of the 1/1, 5/1 and 10/1 copolymers and of the products formed after gelation had occurred, with and without D.C.M.B. present. Figures 77 and 78 show the spectra of the 1/1 copolymer and of the product formed after gelation with no D.C.M.B. present. Identical trends were observed with the other copolymer systems and no differences could be detected in the spectra of the gelled products, whether formed in the absence or presence of D.C.M.B. All spectra were identical in the region 1,800 $cm.^{-1}$ to 4,000 $cm.^{-1}$ and so this range was ommitted from Figures 77 and 78. The spectra of the gelled products are not well defined owing to the difficulty of reducing the polymers to a very fine powder and the spectrum shown in Figure 78 was only obtained after extensive grinding. Solution spectra could not, of course, be obtained due to the complete insolubility of the polymers after gelation.

Figure 77 is basically similar to the spectrum of poly(methyl methacrylate),[116] with additional absorption bands at 1,600, 760 and 700 $cm.^{-1}$ due to the aromatic nuclei present in the 1/1 styrene/methyl methacrylate copolymer. In Figure 78 almost all the absorption bands below 1,000 $cm.^{-1}$ have disappeared except the aromatic out of plane deformations below 800 $cm.^{-1}$, which are present in the original copolymer. This may be due to poor resolution resulting from the form of the sample. The spectrum of the 1/1 copolymer shows a carbonyl absorption band at 1,720 $cm.^{-1}$, as expected for an ester. However, Figure 78 shows an additional absorption at 1,680 $cm.^{-1}$ which is the wavenumber at which an aryl ketone would vibrate. In addition, the absorption bands due to C-O

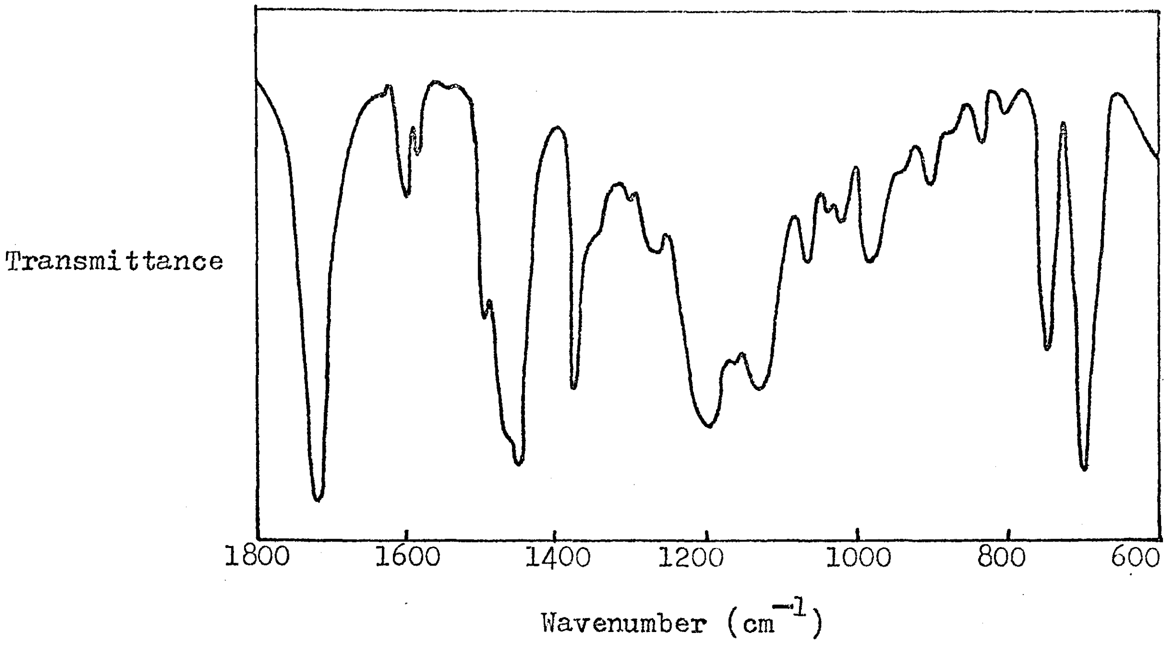


Figure 77. Infra-red Spectrum of the 1/1 Styrene/Methyl Methacrylate Copolymer.

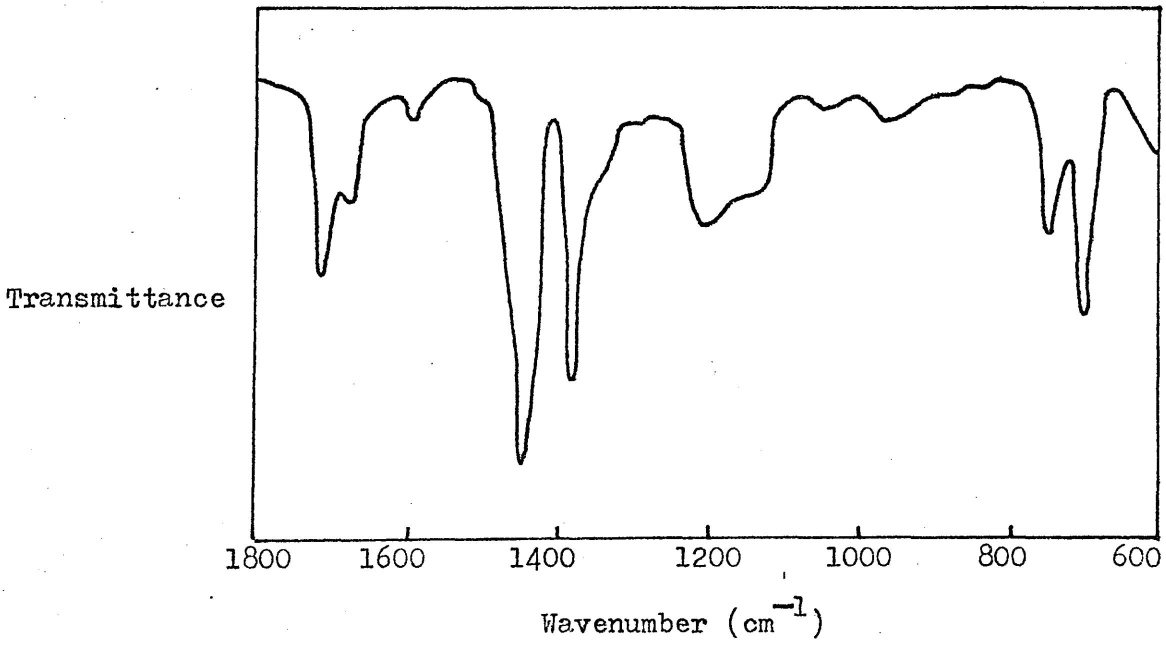


Figure 78. Infra-red Spectrum of the 1/1 Styrene/Methyl Methacrylate Copolymer after Gelation.

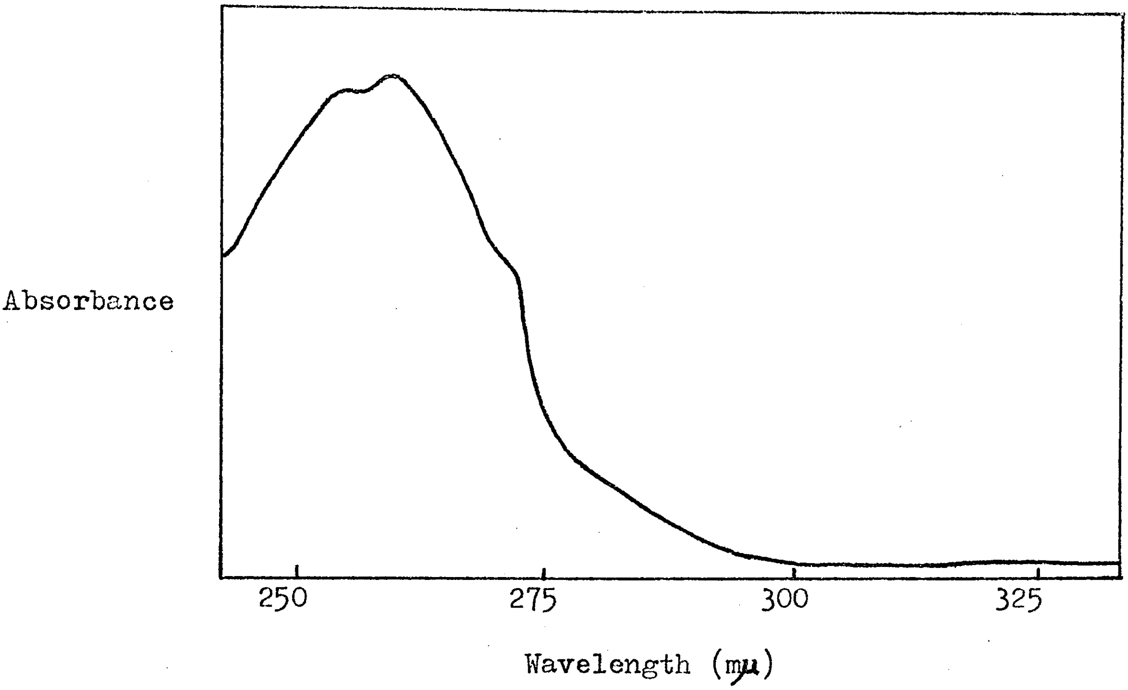


Figure 79. Ultra-violet Spectrum of the 5/1 Styrene/Methyl Methacrylate Copolymer.

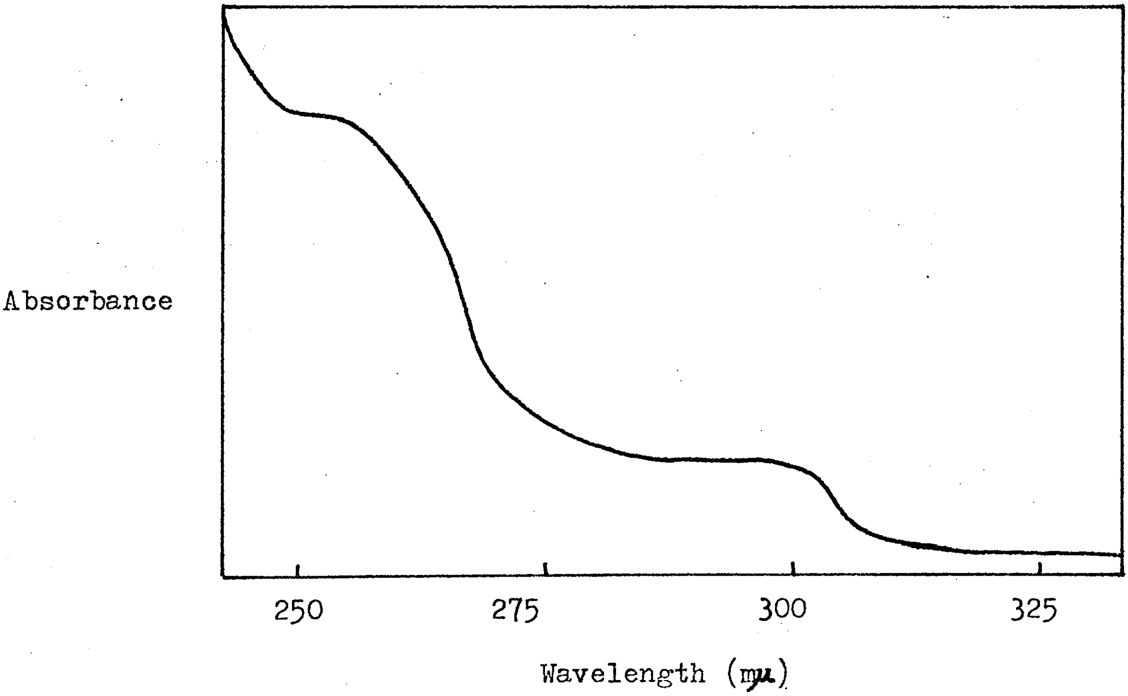
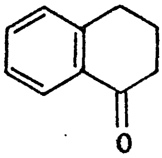


Figure 80. Ultra-violet Spectrum of the 5/1 Styrene/Methyl Methacrylate Copolymer Immediately Prior to Gelation.

stretching at 1,130 and 1,200 $cm.^{-1}$ have decreased in intensity relative to the $-CH_2-$ backbone deformation bands at 1,380 and 1,450 $cm.^{-1}$ All this is further evidence for the presence of the cyclic units proposed earlier. The infra-red spectra of the products formed after gelation, with D.C.M.B. present, showed no evidence for the existence of the 'expected' type of crosslink. This is consistent with the results obtained for polystyrene itself.

Ultra-violet spectra of the three copolymers and the corresponding products formed before the onset of gelation were obtained as described in Chapter 2. Spectra of the gelled products could not be obtained due to insolubility and it was found impossible to obtain any quantitative data, since the products formed even after relatively short reaction times were not completely soluble. Figures 79 and 80 show the ultra-violet spectra of the 5/1 copolymer and the 5/1 copolymer precipitated just short of the gel point, respectively. Similar spectra were obtained for the other two copolymer systems investigated.

Figure 80 shows two absorptions, not present in Figure 79. Below 250mμ, inaccuracy arises due to absorption of energy by the solution under investigation but it can be seen that in the case of the unreacted copolymer, the absorbance decreases whereas in the acylated copolymer, the absorbance increases. There is also an additional absorption band at approximately 290mμ in Figure 80. The chromophore,



has two absorption maxima,[117] at 248mµ ($\in$ = 12,600) and 292mµ ($\in$ = 1,800). Although the extinction coefficients could not be calculated in the case of the partially reacted copolymer, due to insolubility, the fact that two new absorption maxima have appeared in the positions predicted from comparison with tetralone, shows that the reacted copolymer must have chromophores similar to those present in tetralone. Thus, ultra-violet spectroscopy has provided further evidence for the Friedel-Crafts acylation reaction between the methacrylate groups and the ortho position of the styrene nuclei to form aryl ketones.

In the crosslinking reaction between polystyrene and D.C.M.B., quantitative measurement of the degree of crosslinking was determined from the absorbance at 276mµ in the ultra-violet spectrum. However, in the reactions between styrene/methyl methacrylate copolymers and D.C.M.B., the absorbance at 276mµ is masked by the more intense absorbance due to the aryl ketone at 292mµ, and so this method could no longer be used to estimate the degree of crosslinking.

As the products of the reactions involving styrene/methyl methacrylate copolymers in the presence of stannic chloride showed a tendency towards insolubility from the commencement of the reaction, N.M.R. spectra could not be obtained.

b) Copolymers of Methyl Methacrylate and Substituted Styrenes.

It has been shown in the previous section that copolymers of methyl methacrylate and styrene, in the presence of D.C.M.B. and stannic chloride, undergo a Friedel-Crafts acylation reaction between a methacrylate ester group and an adjacent styrene nucleus and also a Friedel-Crafts crosslinking alkylation reaction between D.C.M.B. and the styrene nuclei. The system may be simplified by performing the reaction in the absence of D.C.M.B., so that only the acylation reaction may occur. Supplementary information regarding the acylation reaction should be made available by studying the effect of substituents in the styrene nuclei of the styrene/methyl methacrylate copolymers upon the rate of the acylation reaction.

The copolymers listed in Table 22 were prepared and purified as described in Chapter 2 by a free radical mechanism using the reactivity ratios[89] listed in Table 23. As the reactivity ratios for the copolymer of 2,6-dimethyl styrene and methyl methacrylate were not available, the values for styrene and methyl methacrylate were used. The compositions of all the copolymers were checked after preparation by elemental analysis and the values obtained are listed in Table 22.

Reaction mixtures were prepared containing 4g. of each copolymer in turn with 10 ml. of a 0.87M stannic chloride solution in D.C.E., made up to 20 ml. with D.C.E. They were allowed to react at 60°C in an atmosphere of nitrogen as described in Chapter 2. In each case, the colourless solution darkened as the reaction proceeded, becoming more and more viscous until, at the gel point, a dark brown tar remained. The relative rates of reaction of the copolymers were estimated by noting the time required for gelation. Although this does not give an exact value of the rate, it is sufficient to show general trends. Results are presented in Table 24.

The effect of the substituents under investigation on electrophilic aromatic substitution can be predicted by the inductive and resonance effects.[118] Since no acylation reaction occurs in the 2,6-dimethyl styrene copolymer, the acylation reaction must occur at the ortho position of the styrene nucleus. Also, synthesis of the acylated product using 'Fieser' models shows that due to strain, the acylation reaction can only occur at the ortho position. The substituents used are all ortho

Table 23.

Reactivity Ratios for the Copolymerisation of Methyl Methacrylate (r_A) with Substituted Styrenes (r_B) at 60°C.

Substituted Styrene	r_A	r_B
styrene	0.47	0.50
m-chloro styrene	0.47	0.91
p-chloro styrene	0.42	0.89
p-methoxy styrene	0.29	0.32
m-methyl styrene	0.53	0.49
p-methyl styrene	0.41	0.44
2,6-dimethyl styrene	-	-

Table 24.

Relative Rates of Acylation of the Methyl Methacrylate/Substituted Styrene Copolymers.

Copolymer	Time for Gelation (days)
Poly(methyl methacrylate-co-m-methyl styrene)	9
Poly(methyl methacrylate-co-p-methoxy styrene)	10
Poly(methyl methacrylate-co-p-methyl styrene)	13
Poly(methyl methacrylate-co-styrene)	14
Poly(methyl methacrylate-co-p-chloro styrene)	15
Poly(methyl methacrylate-co-m-chloro styrene)	17
Poly(methyl methacrylate-co-2,6-dimethyl styrene)	-

and para directing towards further substitution and so if a substituent is present in the meta position of the styrene nucleus in the copolymer, then the rate of acylation should be faster than if the same substituent is present in the para position. This is observed in the case of the methyl substituents but not in the case of the chloro substituents.

Methoxy substituents activate benzene nuclei more strongly than methyl substituents and chloro substituents deactivate the nuclei, so that the rate of acylation of chloro substituted styrenes should be slower than for styrene itself. Thus, the order of reactivity for acylation should be,

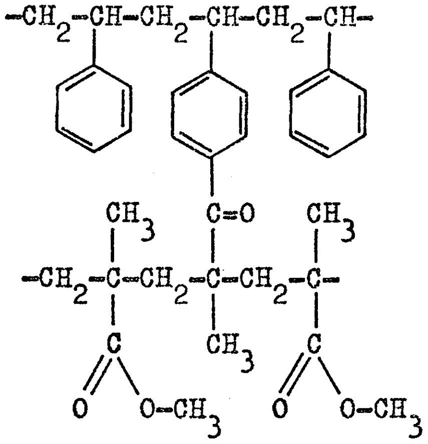
$$-O-CH_3 > -CH_3 > -H > -Cl$$

and this is observed as shown in Table 24.

These results show that with one exception the observed rate of the Friedel-Crafts acylation reaction agrees with the theoretical predictions, with respect to the activating ability of substituents and their positions on the styrene nucleus.

c) Mixtures of Poly(methyl methacrylate) and Polystyrene.

In the previous two sections the Friedel-Crafts acylation reaction which has been discussed is the intramolecular condensation between a methacrylate ester group in a copolymer and the styrene nucleus of an adjacent unit in the chain. However, there is no reason why intermolecular condensation could not occur between styrene nuclei and methacrylate groups on different chains or between aromatic nuclei and ester groups on distant sections of the same copolymer molecule, which happen to be in the correct conformation, due to coiling. It should be possible to study the intermolecular reaction alone by allowing mixtures of homopolymers of styrene and methyl methacrylate to react in the presence of stannic chloride. The expected reaction product would be a polymer with the following crosslinked structure,



Polystyrene and poly(methyl methacrylate) were synthesised and purified as described in Chapter 2. 1g. of an equimolar mixture of polystyrene and poly(methyl methacrylate) was dissolved in 5 ml. of a 0.87M stannic chloride solution in D.C.E. and allowed to react at 60°C in an atmosphere of nitrogen. The colourless solution darkened, became cloudy and the viscosity increased as the reaction proceeded until a dark brown gel was formed after 72 hours. Five identical reaction mixtures were prepared and allowed to react under identical conditions, for different times, short of gelation. Each polymer was precipitated into a 50 % methanol/distilled water mixture and reprecipitated from chloroform.

Number average molecular weights of the starting mixture and the reaction products were measured as described in Chapter 2, and as the reaction which occurs is essentially similar to the polystyrene crosslinking reaction described in Chapter 4, an exponential increase in molecular weight with reaction time was expected, by comparison with the results obtained for the polystyrene/D.C.M.B. system. However, the results shown in Table 25 indicate definite differences between the two systems. It was stated earlier that the cloudiness of the solution increased as the reaction proceeded. This may indicate that either the reaction products were precipitating from the solution, as they were formed, or that microgel was being produced well before the gel point. If the reaction products are insoluble after small degrees of reaction, then the molecular weights obtained will be those of the starting mixtures and if microgel is present then the concentrations of the reaction products in the molecular weight solutions will be inaccurate.

Infra-red spectra of the reacting solution were identical to those of the initial mixture and spectra of the solid products could not be obtained due to the resilience and complete insolubility of these products. This strengthens the argument that the molecular weights measured earlier are not representative of the extent of the reaction. It must be assumed, therefore, from the darkening of the reacting solution, the increasing cloudiness of the solution, the increasing viscosity of the solution, the formation of a gel and the unmanageability of the products that the crosslinking reaction is occurring. Once a crosslink has formed, it may be that the two chains are held in the correct position for reaction at many more sites, with the result that a ladder type polymer is being formed. This would account for the observed properties of the reaction products.

7.3 Thermal Analysis of Styrene/Methyl Methacrylate Copolymers.

Both polystyrene and poly(methyl methacrylate) undergo thermal depolymerisation to give monomer. Due to the presence of the tertiary hydrogen in polystyrene, however, intramolecular transfer occurs,

Table 25.

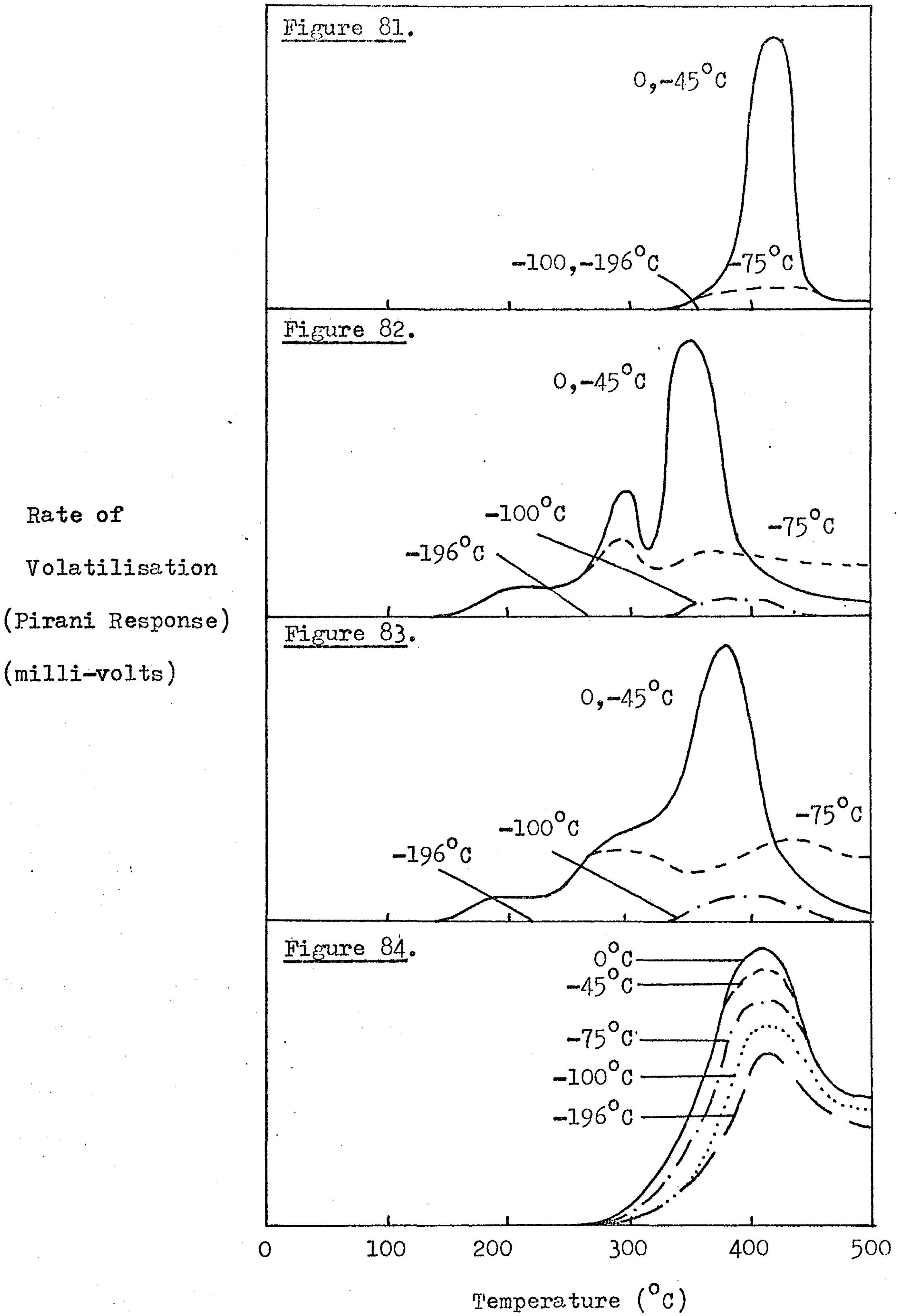
Molecular Weights of the Soluble Products of the Acylation Reaction between Polystyrene and Poly(methyl methacrylate).

Reaction Time (hours)	$\overline{M}_n$
0	11,500
6	7,200
25	insoluble in toluene
30	insoluble in toluene
48	11,000
54	3,600

Table 26.

Relationship between Polymer Composition and Degradation Temperature measured by D.C.T.V.A.

Polymer	T_{max} (°C)
Polystyrene	426
Poly(methyl methacrylate)	(294) 356
5/1 Methyl Methacrylate-Styrene Copolymer	379
5/1 Copolymer after Gelation	408



Figures 81 to 84. D.C.T.V.A. Thermograms of (81) Polystyrene, (82) Poly(methyl methacrylate), (83) 5/1 Styrene/Methyl Methacrylate Copolymer and (84) 5/1 Styrene/Methyl Methacrylate Copolymer after Gelation.

leading to the formation of dimer, trimer and higher products,[88] in addition to monomer. The thermal stability of poly(methyl methacrylate) is very sensitive to the nature of the end group and thus to the molecular weight[119] but polystyrene is independent of these factors. T.V.A. shows the thermal degradation of polystyrene to be a single stage process, whereas the T.V.A. thermogram of poly(methyl methacrylate) has two peaks. The peak at the lower temperature is due to initiation of degradation at unsaturated terminal structures and the peak at the higher temperature is due to initiation by random scission. Polystyrene shows higher thermal stability.

In copolymers of styrene and methyl methacrylate,[120] where the concentration of styrene is higher than 1/4, the lower temperature peak disappears leaving a single peak which is intermediate between the higher T_{max} for poly(methyl methacrylate) and the polystyrene T_{max}. The temperature at which the maximum rate of volatilisation occurs increases with styrene content of the copolymer. At styrene contents of less than 1/4, the lower T_{max} peak of methyl methacrylate is reduced but does not disappear completely.

The thermal degradative behaviour of the copolymers is, therefore, intermediate between the individual homopolymers but styrene is found to have a disproportionately large stabilising effect upon poly(methyl methacrylate). Grassie and Farish[121] reasoned that the copolymers contain fewer unstable end structures due to cross-termination during copolymerisation and McNeill[119] has argued further that a 'cage effect' is operating when a pair of polystyryl radicals are produced after initial scission between a pair of methyl methacrylate units in the copolymer chain, preventing further unzipping. This is a logical progression, since Grassie and Grant[122] have shown that polystyryl radicals produced below 300°C do not depolymerise until the degradation temperature for polystyrene is attained.

The effect of the Friedel-Crafts acylation upon the thermal stability of the styrene/methyl methacrylate copolymers was determined by T.V.A. 50mg. powder samples were heated at a rate of 10°C/min. using the technique described in Chapter 2.

D.C.T.V.A. thermograms of polystyrene, poly(methyl methacrylate), the 5/1 methyl methacrylate/styrene copolymer and the identical copolymer after gelation are shown in Figures 81, 82, 83 and 84, respectively. The single stage degradation of polystyrene, the two stage degradation of poly(methyl methacrylate) and the limiting rate at -75°C due to styrene and methyl methacrylate production,[88] respectively, are all well defined. The T_{max} values for each sample are presented in Table 26 and it can be seen that the T_{max} for polystyrene is at a considerably higher temperature than either T_{max} for poly(methyl methacrylate). Figure 83 shows results similar to those obtained by McNeill[119] for a 4/1 methyl methacrylate/styrene copolymer, the rate of initiation at terminal structures being drastically reduced and the temperature at which the maximum rate of volatilisation for random initiation of degradation occurs moving to a higher value. The limiting rate effect at -75°C due to styrene and methyl methacrylate production is again well defined.

The thermogram for the 5/1 copolymer which has been allowed to gel due to the Friedel-Crafts acylation reaction is identical to the thermogram obtained when the identical copolymer is allowed to gel as a result of the acylation reaction and the crosslinking reaction with D.C.M.B. Figure 84 shows the product of the acylation alone and it can be seen that the temperature of the maximum rate of volatilisation is higher than that of the copolymer itself. There is no limiting rate effect at -75°C in the acylated product, indicating that if styrene and methyl methacrylate are being produced then only trace quantities can be present. The presence of the cyclic acylated structures in the copolymer chain must, therefore, be preventing the depolymerisation process. Since large amounts of non-condensables are produced during degradation of the acylated copolymer, this suggests that random scission is occurring with the elimination of highly volatile products, such as carbon monoxide, methane and hydrogen.[88] Examination of the cyclised structure indicates the feasibility of this assumption.

T_{max} for the acylated product of the 5/1 copolymer is approximately equal to the T_{max} obtained by McNeill[119] for the 1/1 styrene/methyl methacrylate copolymer. Therefore, in addition to the increasing styrene content of a copolymer increasing the thermal stability, the quantity of acylation present must also increase the thermal stability. This further stabilisation of the copolymer is probably due to the presence of cyclised structures in the chain preventing depolymerisation, even more effectively than styrene and causing the T_{max} to move to a higher temperature. Also the complete absence of the T_{max} due to end initiation of degradation, in Figure 84 compared with the slight shoulder in Figure 83, indicates that if end initiation of degradation does occur due to a small percentage of unsaturated structures in the 5/1 copolymer, then depolymerisation is quickly blocked by the cyclised structures.

7.4 Summary.

10/1, 5/1 and 1/1 copolymers of methyl methacrylate and styrene were allowed to react with D.C.M.B. in the presence of stannic chloride, in D.C.E. at 60°C under nitrogen. Colouration in the products suggested that another reaction is occurring, in addition to the Friedel-Crafts alkylation between D.C.M.B. and the styrene nuclei which yields white products. The experiments were repeated in absence of D.C.M.B. and a slower reaction produced dark brown products. Spectroscopic analysis indicated that a Friedel-Crafts acylation between adjacent methacrylate ester groups and styrene nuclei occurs, resulting in cyclic ketonic structures. Experiments with 2,6-dimethyl styrene/methyl methacrylate copolymers suggested that the acylation reaction occurs at the ortho position of the styrene nucleus.

The rate of the acylation reaction is affected in the predicted manner by the presence of activating and deactivating substituents in the styrene ring and a brief investigation into the intermolecular acylation involving homopolymers of styrene and methyl methacrylate showed that crosslinks are formed by an identical condensation. The thermal stability of the acylated copolymers is increased with respect to the copolymers due to a change in the mechanism of the degradation.

CHAPTER EIGHT.

GENERAL DISCUSSION AND REVIEW.

8.1 Introduction.

In this chapter the results and discussions presented in the previous chapters are summarised and correlated with a view to establishing the mechanism of the polystyrene/D.C.M.B. condensation. The effects of crosslinking on the physical properties of polystyrene and the effect of the cyclising acylation on the properties of styrene/methyl methacrylate copolymers are reviewed.

8.2 Kinetics of Crosslinking Polystyrene.

It has been demonstrated in Chapter 4 that the condensation between polystyrene and D.C.M.B., catalysed by stannic chloride, to produce crosslinked polystyrene can be subdivided into intermolecular reactions, which link distinct polystyrene chains and intramolecular reactions, which link remote segments of the same polymer molecule. The results obtained for the overall reaction are a summation of these two independent reactions and the rate equations observed are as follows,

Overall Reaction.

$$\text{Rate} = k_N(\text{D.C.M.B.})(\text{SnCl}_4)$$

Intermolecular Reaction.

$$\text{Rate} = k_n(\text{D.C.M.B.})(\text{Polystyrene})(\text{SnCl}_4)$$

Intramolecular Reaction.

$$\text{Rate} = \frac{k_{N-n}(\text{D.C.M.B.})(\text{SnCl}_4)}{(\text{Polystyrene})}$$

Although the experimental value for the order of the overall reaction with respect to the initial D.C.M.B. concentration was found to be 0.65, the discussion in Chapter 4 demonstrated that the true value is probably unity, as shown above, by analogy with the separate intermolecular and intramolecular reactions, which were observed to show first order dependence upon the initial D.C.M.B. concentration. Also, the shape of the reaction rate versus initial D.C.M.B. concentration curve, indicated the possibility of a competing reaction, which could not, unfortunately, be detected.

The independence of the rate of the overall reaction of the initial polystyrene concentration was explained by regarding the overall reaction as the resultant of the intermolecular and intramolecular reactions which were found to show orders of 1 and -1, respectively, with respect to the initial polystyrene concentration. An explanation for the order of -1, with respect to the initial polystyrene concentration for the intramolecular reaction, follows from the coiling properties of polymers causing increasing inhibition of the diffusion of the reactants into the polystyrene molecules as the initial polystyrene concentration increases.

It can be seen from these rate equations that excluding the unexpected results already mentioned, first order dependence upon the initial concentration of each reactant was observed. These were the expected results, by analogy with the benzene/D.C.M.B. condensation[16] and the toluene/D.C.M.B. condensation investigated in Chapter 5 as a model for the polystyrene/D.C.M.B. system. The rate equation for the toluene/D.C.M.B. reaction was found to be,

$$\text{Rate} = k_T(\text{D.C.M.B.})(\text{Toluene})(\text{SnCl}_4)$$

Spectroscopic, thermal and elemental analysis of the products of the polystyrene/D.C.M.B. condensation showed complete absence of pendant chloromethyl groups, resulting from partially reacted D.C.M.B. molecules. This indicates that the second chloromethyl group in D.C.M.B. is much more reactive than the first, due to the absence of a second strongly electronegative centre as in D.C.M.B. and this is in agreement with the results observed in the benzene/D.C.M.B. condensation.[16] Reaction of the first chloromethyl group with polystyrene was, therefore, assumed to be the rate determining step in the crosslinking reaction and the reaction of the second chloromethyl group with another styrene nucleus was regarded as having little effect upon the kinetics.

A comparison of the relative rates of the reaction of D.C.M.B. with various substituted aromatic nuclei was presented in Chapter 5. This demonstrated the order of reactivity predicted by the relative activating abilities of the substituents already present in the aromatic nuclei. Polystyrene was found to be less reactive than the primary aromatic nuclei due to steric effects.

Although the overall rate of crosslink formation is constant, the rate of intermolecular crosslinking is high initially and decreases approaching the gel point and the rate of intramolecular crosslinking is low initially and increases rapidly in the region of gelation. This was explained in Chapter 4 as resulting from crosslinking which tends to make the molecules more spherical and so in the later stages of the reaction the intramolecular reaction is predominant, although at this stage relatively few intermolecular crosslinks are required to have a major effect upon the molecular weight.

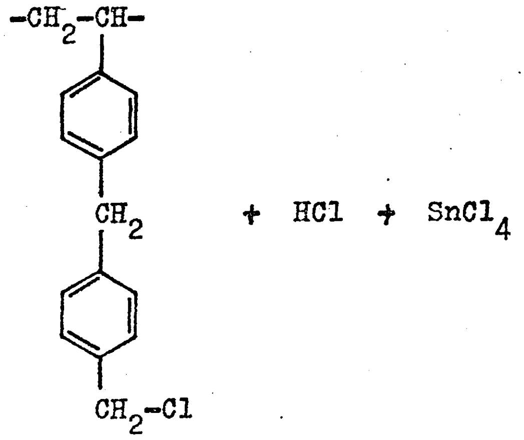
8.3 Mechanism of the Polystyrene/D.C.M.B. Condensation.

The important reaction occurring under the conditions chosen, is the intermolecular condensation between polystyrene and D.C.M.B., catalysed by stannic chloride. This reaction has been found to show first order dependence upon the concentrations of the reactants and the catalyst and this can be interpreted in terms of the following mechanism.

In reactions of this type, formation of a complex between the catalyst and chloro-compound is generally accepted as being the first step. Interaction between an electronegative chlorine atom of D.C.M.B. and an electropositive tin atom results in the following complex,

$$Cl{-}CH_2{-}C_6H_4{-}CH_2^{\delta+}\cdots\cdots\cdots\cdots\cdots SnCl_5^{\delta-}$$

Reaction of an aromatic nucleus in polystyrene with this complex gives initially,



and the faster reaction of the second chloromethyl group with another styrene nucleus, by an identical mechanism, yields the crosslinked product. Grassie and Meldrum[16] have demonstrated that, in reactions of this type, the establishment of an equilibrium concentration of the complex is rapid compared with the rate of the reaction of the complex with aromatic nuclei. The absence of an induction period in the reaction curves indicates that this is also true for the system under consideration and so the reaction may be represented by,

$$\text{D.C.M.B.} + \text{SnCl}_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Complex}$$

$$\text{Complex} + \text{Polystyrene} \xrightarrow{k_3} \text{Products}$$

In the stationary state,

$$\frac{d(\text{Complex})}{dt} = 0 = k_1(\text{D.C.M.B.})(\text{SnCl}_4) - k_2(\text{Complex}) - k_3(\text{Complex})(\text{Polystyrene})$$

$$(\text{Complex}) = \frac{k_1(\text{D.C.M.B.})(\text{SnCl}_4)}{k_2 + k_3(\text{Polystyrene})}$$

$$\text{Rate of the Reaction} = k_3(\text{Complex})(\text{Polystyrene})$$

$$= \frac{k_1k_3(\text{D.C.M.B.})(\text{Polystyrene})(\text{SnCl}_4)}{k_2 + k_3(\text{Polystyrene})}$$

Assuming that $k_2 \gg k_3(\text{Polystyrene})$ then,

$$\text{Rate of the Reaction} = \frac{k_1k_3}{k_2}(\text{D.C.M.B.})(\text{Polystyrene})(\text{SnCl}_4)$$

This mechanism accounts for the dependence of the rate of the intermolecular condensation upon the first power of the concentration of each reactant, as observed in Chapter 4 and an identical mechanism would account for the first order dependence of the reaction rate with respect to the concentration of each reactant, observed for the toluene/D.C.M.B. condensation, investigated in Chapter 5. However, the independence of the rate of the overall reaction of the polystyrene concentration cannot be explained by this mechanism since this would require that $k_2 \ll k_3(\text{Polystyrene})$ which is unlikely as an induction period was not observed. Similarly, the dependence of the intramolecular reaction rate upon the inverse of the polystyrene concentration cannot be interpreted by this mechanism, although qualitative explanations have been proposed.

8.4 Temperature Dependent Properties of Crosslinked Polystyrene.

The results of the investigations described in Chapter 6 have indicated that the structure of crosslinked polystyrene has two completely diverse effects upon the properties of the polymer.

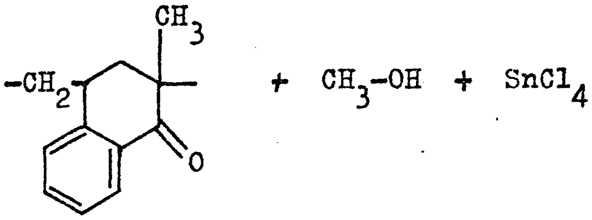
An increase in the glass transition temperature was observed with an increase in the degree of crosslinking. This direct proportionality is due to the additional energy which is required for segmental motion in the sterically hindered crosslinked network.

Concurrently, a less advantageous result was observed during thermal degradative studies of the crosslinked polystyrenes. The crosslinked polymers showed lower thermal stability than linear polystyrene. This has been associated with the strain present in crosslinked molecules and it has been proposed that preferential scission is initiated either at a position in the backbone, in the vicinity of a branch point or in the crosslink itself.

8.5 Styrene/Methyl Methacrylate Copolymer Cyclisation Reaction.

In addition to catalysing the crosslinking of styrene/methyl methacrylate copolymers by D.C.M.B., stannic chloride also catalyses a cyclisation reaction between a methacrylate ester group and the ortho position of the styrene nucleus, adjacent to it in the copolymer chain. The Friedel-Crafts acylation producing these cyclic structures would probably occur by complex formation similar to that described for the condensation of D.C.M.B. with aromatic nuclei,

Reaction of this complex with the ortho position of the adjacent styrene nucleus would yield the cyclised product,



Although no kinetic evidence was collected, it would be reasonable to suggest that since the acylation is similar to the polystyrene/D.C.M.B. alkylation, the mechanistics could be represented as described previously.

The resultant cyclised structure formed in these copolymers, due to this Friedel-Crafts acylation, was found to enhance the thermal stability of the copolymers with respect to their parent copolymers, as the cyclic structures cause a change in the degradation mechanism, from essentially depolymerisation to random scission. These deductions were made from an examination of the differences in the D.C.T.V.A. traces of the copolymers and the corresponding cyclised products. Another factor contributing to the enhanced stability of the cyclised product must be the fact that these are really partial ladder polymers.

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