

Friedel–Crafts crosslinking methods for polystyrene modification:

1. Preparation and kinetics

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A two-step polymerization and grafting–crosslinking reaction was developed for modification of polystyrene. Styrene was first polymerized in dichloroethane at 25°C using SnCl₄ as catalyst. The cationically prepared polystyrene was then grafted with 1,4-dimethyl-2,5-dichloromethyl benzene in dichloroethane at 50°C in a Friedel–Crafts reaction system. The kinetics of the reaction were followed by titrating the evolved HCl from the reaction system. The maximum reaction rate was found to vary with both the initial concentration of 1,4-dimethyl-2,5-dichloromethyl benzene and the initial concentration of SnCl₄. Determination of the concentration of junctions of the grafted polystyrene samples and analysis of their u.v. spectra were used to determine the progress of the reaction, and to propose a reaction mechanism.

Keywords Crosslinked polystyrene; crosslinking; Friedel–Crafts polymerization; grafting; junctions; polystyrene; chromatographic resins

INTRODUCTION

This contribution seeks to study new methods of preparation of grafted and crosslinked polymers of aromatic character through the use of a two-step polymerization and grafting–crosslinking reaction. The polymer studied as a model for this reaction was cationically prepared polystyrene. In contrast to linear polystyrene, grafted polystyrene has a branched structure and it is a precursor of the crosslinked polystyrene network.

A crosslinked polystyrene structure can be formed by copolymerization of styrene and another monomer containing two or more reactive groups. It can also be obtained when polymerization of styrene is followed by a crosslinking reaction, in which another monomer or crosslinking agent is reacted with the polystyrene chains to form a network structure. The most widely used crosslinking monomer for polystyrene is divinylbenzene (DVB).

Since both the polymerization of styrene and the subsequent crosslinking reaction studied in this work were cationic processes, it was convenient from an experimental point of view to carry out the entire process in one step starting from styrene. Although it was shown that a one-step process was difficult to obtain due to the kinetics of the two reactions, there were still advantages in carrying out the two reactions sequentially in the same reactor. The most notable advantages were: (i) use of the same catalyst; (ii) use of the same solvent; and (iii) crosslinking could be commenced after a predetermined yield or molecular weight distribution was obtained.

Friedel–Crafts polymerization of styrene

Cationic polymerization of styrene gives relatively low

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molecular weight polymers (M_n of 1000–10 000) at temperatures of 30°C, and higher molecular weight polymers (M_n up to 100 000) at low temperatures of approximately –80°C¹.

Friedel–Crafts metal halides are the most widely used group of cationic polymerization catalysts. Numerous kinetic studies have been reported using AlCl₃², BF₃³, SnCl₄^{4,5}, and TiCl₄⁶. Experimentally, the most favoured catalysts have been SnCl₄ and TiCl₄, since they usually give relatively slow and controllable polymerization rates¹. However, the molecular weight of the polymer obtained by these catalysts may not be as high as that with the more active metal halide catalysts. The following sequence of reactivity has been given^{1,3} for the polymerization rate in benzene and dichloroethane, TiCl₄ > SnCl₄ > FeCl₃ > BF₃. Yield, molecular weight, and polymerization rate generally do not follow the same sequence.

With some exceptions, the pure metallic halide is inactive as a catalyst in the polymerization of styrene and a cocatalyst (or promoter) is required to activate the catalyst. The cocatalyst may be any protonic acid or water. Cationic polymerization of styrene by stannic chloride in dichloroethane solution can occur in the absence of water⁴ with *t*-butyl chloride serving as a cocatalyst. Grassie and Meldrum⁷ have demonstrated that reactions of Friedel–Crafts crosslinking monomers using stannic chloride catalysts do not require external cocatalyst since this is formed during the reaction (HCl). These reactions are similar to styrene polymerizations. A maximum rate is observed when the H₂O/SnCl₄ molar ratio is unity. At higher concentrations of water, the stannic chloride is precipitated from solution as a hydrate, while at lower concentrations of water the concentration of the catalytically active SnCl₄/H₂O complex is reduced in favour of the less active SnCl₄.

Chlorinated solvents are commonly used, offering a

range of polarities from the nonpolar CCl_4 to the moderately polar dichloroethane. Pepper⁵ has shown that dichloroethane exhibits cocatalytic behaviour in cationic polymerization, and Grassie and Meldrum^{8,9} have shown that it accelerates the reaction between crosslinking monomers of polystyrene and benzene.

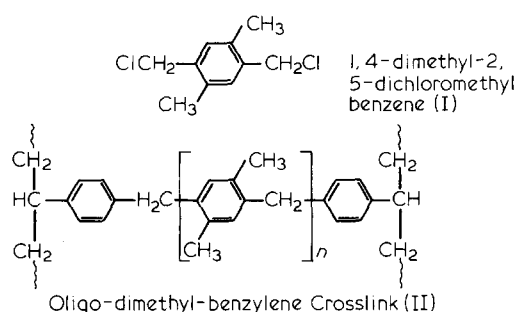
Friedel-Crafts crosslinking of polystyrene

Monomers or oligomers with aromatic rings in the main chain are more desirable than divinyl benzene as crosslinking agents of polystyrene, because they have been found to lead to crosslinked networks of controlled mesh size under certain experimental conditions^{10,11}. This is especially true when the rings are linked through the *p*-positions. Friedel-Crafts crosslinking of polystyrene was first observed as a competing reaction of certain chloromethylations of polystyrene^{2,12}.

Grassie and his associates¹³ were the first to propose a new Friedel-Crafts-based crosslinking reaction of polystyrene, after their successful copolymerization of 1,4-dichloromethyl benzene with compounds having either carbocyclic or heterocyclic aromatic character. Since the introduction of this method, a number of kinetic studies have been made^{10,11,13-21}. Crosslinking agents or monomers used in these studies included benzyl chloride, 1,4-dichloromethyl benzene, 2,5-dimethyl-benzyl chloride, 1,4-dimethyl-2,5-dichloromethyl benzene, 1,4-dichloromethyl-durene, 4,4'-dichloromethyl-diphenylene, and oligo-dimethyl benzylenes with fewer than ten repeating units. Although chlorinated derivatives of aromatic compounds are the most widely used Friedel-Crafts crosslinking agents, studies have been reported also with crosslinking agents with $-\text{OCH}_3$ or $-\text{OCOCH}_3$ groups substituting for the chlorine atoms¹⁰. Of these crosslinking monomers, the most extensive work has been done on the 1,4-dichloromethyl benzene reactions by Grassie and his associates^{13,16,17}.

Among these crosslinking agents, 1,4-dimethyl-2,5-dichloromethyl benzene (monomer I) has been shown to be a desirable agent for crosslinking of polystyrene, as analysed before by Peppas and Valkanas¹⁰.

Its structure, preparation, and properties have been studied extensively^{22,23}. It can self-condense to form linear bridges when used for grafting or crosslinking polystyrene in reaction in the presence of H_2SO_4 or HClO_4 as catalysts and in solvents such as acetic acid or butyl acetate^{10,20}. Thus, polymers of type II can be produced with increased molecular weight and improved thermal properties.



Here we present studies on the kinetics and mechanism of grafting-crosslinking reactions of polystyrene using Friedel-Crafts catalysts and analysis of the molecular weight of the products.

EXPERIMENTAL

Polymerization of styrene

Styrene (99%, Aldrich Chemical Co.) containing 15 ppm of *p*-tertbutylcatechol as an inhibitor was vacuum-distilled at $61^\circ\text{C}/41$ mm Hg to remove the inhibitor and trace amounts of oligomers and polymer. The initial and final 25% of the distilled styrene were discarded. Before each reaction, samples of styrene monomer were mixed with methanol. A white precipitate indicated the presence of oligomer, and the monomer had to be redistilled. The catalyst used was stannic chloride (99.5%, anhydrous, J. T. Baker Chemical Co.), which was introduced into the reacting system as a 0.085 mol l^{-1} solution in dichloroethane.

In a typical polymerization experiment, 47.1 ml dichloroethane, 35.5 ml of 0.085 mol l^{-1} SnCl_4 solution in dichloroethane, and 62.0 ml of styrene were reacted in a four-necked flask for 4 h at $25^\circ \pm 0.5^\circ\text{C}$, under continuous purge of dry nitrogen. The initial concentrations of styrene and SnCl_4 in the reacting system were 3.53 and 0.020 mol l^{-1} respectively.

Grafting and crosslinking of polystyrene

Upon completion of the polymerization reaction, dried nitrogen was passed over the reaction mixture at a rate of 50 ml min^{-1} : (i) to remove the HCl produced by the grafting and crosslinking reaction; and (ii) to minimize the effects of moisture and oxygen on the grafting and crosslinking reaction. After the contents of the reactor had equilibrated at 50°C for approximately 10 min, the grafting-crosslinking agent, 1,4-dimethyl-2,5-dichloromethyl benzene (monomer I, henceforth designated as DMDCB), was introduced into the reactor, and the grafting reaction begun. Techniques of preparation of DMDCB were previously described by Peppas and his associates^{10,19}. Aliquots of the reaction mixture were taken at 30 min intervals until gelation of the polymer occurred, for characterization of the grafted polymer.

A reservoir containing 20 ml of distilled water was used to scrub the HCl produced in the grafting reaction from the nitrogen purge. The reservoir was replaced by fresh solution every 5 min and its contents were titrated against a standardized NaOH solution. From these data the concentration of grafting or crosslinking points (henceforth designated as 'concentration of junctions') was calculated, by taking into consideration that one mole of HCl is evolved for every chloromethylated functional group reacting.

The crosslinking reaction was allowed to proceed until the onset of gelation. At this point the polymer was sufficiently crosslinked that is no longer dissolved in the solvent but rather swelled in it, changing the reaction mixture from a solution to a gel-like mass. Table I reports the conditions that were used in the grafting reaction.

Samples of the reaction solution were taken every 30 min to isolate and purify the polymer for characterization of its properties. The samples were precipitated in methanol, filtered off, dried, and redissolved in pure dioxane. The dioxane solution was poured into a large volume of distilled water and the reprecipitated polymer was filtered off and dried under vacuum at 80°C at 1 mm Hg for 6 h to remove any residual solvent or monomer. The dried polymer was then analysed by ultraviolet spectroscopy.

Table 1 Reaction conditions and concentrations of reactants for grafting-crosslinking reactions

Series	Reaction temperature (°C)	[DMDCB] (mol l ⁻¹)	[SnCl ₄] (mol l ⁻¹)	[Polystyrene] (mol l ⁻¹)	Molar ratio × 10 ² [DMDCB]/[PS]
A	80	0.164	0.021	3.96	4.14
B	70	0.149	0.019	3.56	4.18
C	25	0.161	0.021	3.83	4.20
D	40	0.160	0.021	3.80	4.21
E	50	0.159	0.021	3.80	4.18
F	60	0.158	0.021	3.79	4.17
G	50	0.038	0.021	3.81	1.00
H	40	0.038	0.021	3.85	0.99
J	60	0.038	0.021	3.79	1.00
K	50	0.019	0.021	3.80	0.50
L	50	0.038	0.020	3.53	1.08
M	50	0.071	0.021	3.72	1.92
N	50	0.025	0.020	3.69	0.68
O	50	0.147	0.020	3.67	4.00
P	50	0.283	0.019	3.40	8.32
Q	50	0.038	0.041	3.43	1.11
R	50	0.273	0.018	3.26	8.37
S	50	0.018	0.020	3.60	0.50
T	50	0.037	0.041	3.40	1.09
U	50	0.036	0.079	3.31	1.09
W	50	0.035	0.030	3.26	1.07

To examine whether DMDCB could polycondense under the conditions of this reaction, and in view of previous results with other catalysts and solvents^{10,20}, reactions of DMDCB at 50°, 60° and 70°C were carried out at identical concentrations and with the same solvent as in the grafting-crosslinking reaction, but in the absence of polystyrene. No insoluble product was produced, but the solution was precipitated in methanol, filtered off, dried and analysed by elemental analysis for chlorine. The results were as follows:

Analysis: Calcd. for I: C 59.11%; H 5.91%, Cl 34.98%.
 Calcd. for oligomer of I with $n=2$: C 71.03%;
 H 5.85%, Cl 2.12%.
 Found: C 61.3%; H 6.0%; Cl 32.7%.

It was concluded that under the conditions of this present reaction polycondensation of DMDCB was insignificant and determination of the 'concentration of junctions' could be done as described in this section. These results are somewhat surprising, since in the as yet unpublished work of suspension crosslinking of polystyrene with DMDCB using a concentrated solution of ZnCl₂ as a catalyst (D. Barar and N. A. Peppas), we detected the formation of DMDCB trimers.

Polymer characterization

The average molecular weight and molecular weight distribution of selected samples of polystyrene produced during the polymerization reaction but before the addition of DMDCB, were determined by gel permeation chromatography (Waters Associates 6000 A with refractive index detector) using tetrahydrofuran as a solvent, and five μ -Styragel^R columns (2×10^2 Å, 10^3 Å, 10^4 Å, 10^5 Å). Calibration was done with standard monodisperse polystyrene samples.

Ultraviolet spectra were obtained for solutions of several grafted polymer samples before gelation. Solutions of 0.05 wt% polymer in chloroform were prepared and the u.v. spectra for both linear and grafted polystyrene were obtained for the wavelength range of 2500–3000 Å (Figure 1). The absorption shoulder at 2780

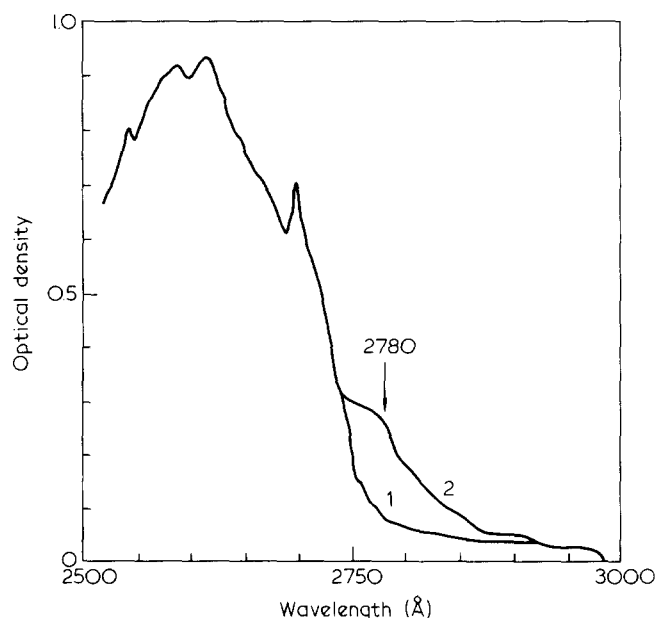


Figure 1 Ultraviolet spectra of linear (1) and grafted (2) polystyrene

Å is characteristic of linear grafting of polystyrene and it is attributed to bond stretching in the *p*-position of the 2,5-disubstituted benzene ring.

¹H-n.m.r. spectra were also obtained for selected grafted polystyrene samples, using trimethylsilane as a standard. Figure 2 shows a typical spectrum and includes identification of important peaks.

RESULTS AND DISCUSSION

Characteristics of polymerization and crosslinking reactions

Before the grafting/crosslinking reaction was studied it was necessary to design the reaction system by determining the conditions for both the polymerization and the crosslinking reaction.

Table 2 Reaction conditions and average molecular weights by cationic styrene polymerization*

Series	Reaction time (h)	Reaction temperature (°C)	[Styrene] (mol l ⁻¹)	\bar{M}_n	\bar{M}_w	Yield (%)
1	1	30	0.773	1800	3700	20.3
2	1	30	0.945	1950	4050	26.7
3	4	25	0.778	4900	10300	—
4	4	25	2.20	12000	24300	66.2
5	4	25	4.00	16100	33500	—
6	4	0	1.23	28600	60050	—
7	4	2	4.00	31700	65300	92.4
8	1	25	3.78	11700	24000	86.7
9	2	25	3.78	—	—	90.6
10	3	25	3.78	—	—	94.1
11	4	25	3.78	12900	26550	97.4

* Catalyst [SnCl₄] = 0.020 ± 0.001 mol l⁻¹

Table 3 Effect of grafting reaction conditions on the concentration of junctions in polystyrene*

Series	[DMDCB] (mol l ⁻¹)	Temperature (°C)	\bar{M}_n at t = 0	Gelation time (min)	Concentration of junctions (x10 ² mol l ⁻¹) at various reaction times (h)							
					0.0	0.5	1.0	2.0	3.0	4.0	5.0	
C	0.161	25	—	>360	0.0	0.03	0.05	0.07	0.14			
D	0.160	40	9600	180	0.0	0.05	0.14	0.65	2.57g			
H	0.038	40	13000	480	0.0	—	0.03	0.14	0.33	1.09	2.50	
E	0.159	50	11100	125	0.0	0.02	0.16	2.55	3.17g			
G	0.038	50	10250	198	0.0	—	0.37	1.68	2.83	3.36g		
F	0.158	60	9100	45	0.0	1.50	4.14g					
J	0.038	60	11550	95	0.0	0.14	1.30	2.64g	3.56g			
B	0.149	70	11200	30	0.0	3.82g						
A	0.169	80	13600	25	0.0	6.95g						

* Catalyst [SnCl₄] = 0.020 ± 0.001 mol l⁻¹; g = gel

The results of styrene polymerization are summarized in Table 2. As expected, the reaction at 30°C produced a polystyrene with a low molecular weight, while the reaction at 0°C produced a polystyrene with a relatively higher molecular weight. The molecular weight distribution as determined by g.p.c. was characteristic of a most probable distribution with polydispersity index ranging between 2.04 and 2.10. To avoid temperature control at subambient temperatures, a polymerization reaction temperature of 25°C was chosen. The results in Table 2 also show a slight dependence of \bar{M}_n and \bar{M}_w on initial monomer concentration. From these results, the initial monomer concentration was restricted to the range of 2.0–4.0 mol l⁻¹. The catalyst concentration was held constant at a value of 0.02 mol l⁻¹.

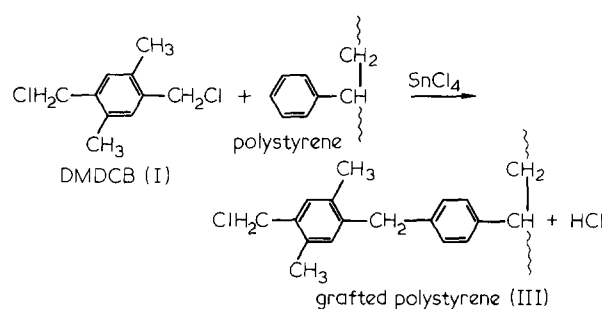
The conversion or yield of polystyrene in the polymerization reaction is a function of reaction time. The conversion results are also presented in Table 2. The reaction is at virtual completion after four hours.

The optimum crosslinking reaction temperature was determined by a series of experiments, which are presented in Table 3. The crosslinking reaction was carried out at various temperatures between 25° and 80°C for two concentrations of DMDCB. It would have been most convenient for the crosslinking reaction to occur at 25°C after the polymerization reaction was complete. However, below 40°C the crosslinking reaction was very slow even at high concentrations of DMDCB. Reactions at temperatures above 60°C occurred so fast that the gelation point was reached in a very short period of time. Desirable residence times were obtained at temperatures

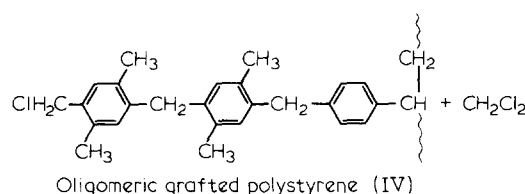
in the 40°–60°C range. A crosslinking reaction temperature of 50°C was chosen for this experimental work.

Kinetics of grafting-crosslinking reactions

The kinetics of the grafting reaction of polystyrene with DMDCB in the presence of SnCl₄ was studied at 50°C. The reaction scheme is shown here.



The remaining chloromethyl group is free to react with either another molecule of DMDCB or another styrene unit of a polystyrene chain to give either of the polymer structures shown below:



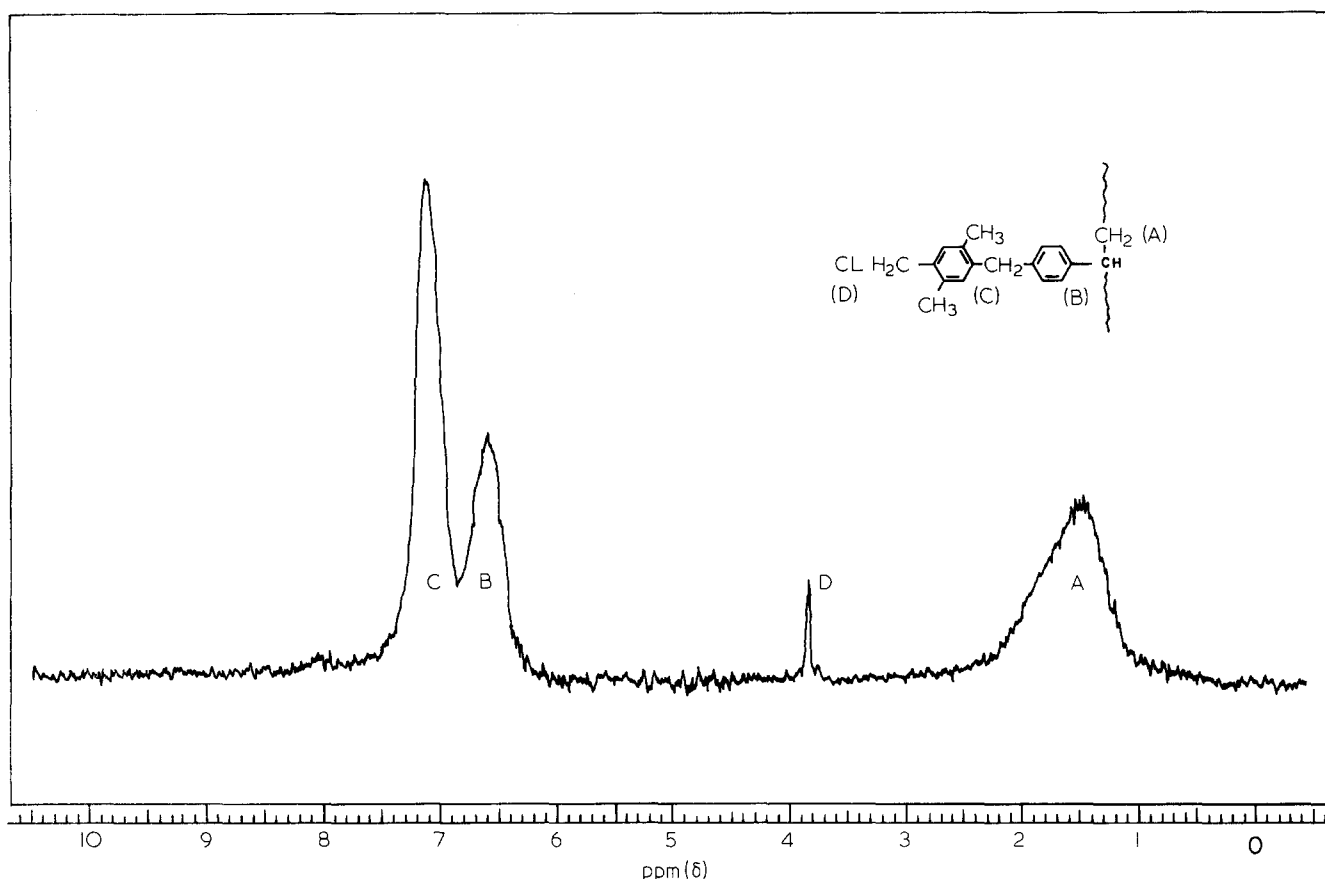
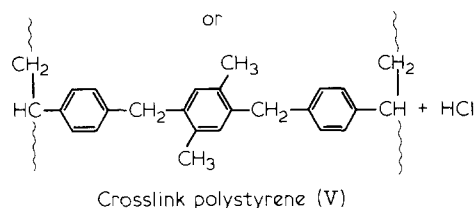


Figure 2 H^1 -n.m.r. spectrum of Friedel-Crafts grafted polystyrene in carbon tetrachloride, using tetramethylsilane as a standard



However, studies discussed in the experimental part showed that polycondensation of DMDCB did not occur under the present reaction conditions. Therefore, structure IV which presents a possible oligomeric grafted polystyrene is not feasible here. We have concluded that the only probable structures of the materials produced were III (for grafted polystyrene) and V (for crosslinked polystyrene).

One molecule of HCl is liberated when DMDCB forms either a grafted junction or a crosslink with the polystyrene. The kinetics of the reaction were studied by following the evolution of HCl as a function of time. Previous studies¹⁶ comparing this method with quantitative ultraviolet spectra analysis showed that these two methods gave consistent results. Also a series of runs without DMDCB confirmed the expectation that no reaction evolving HCl occurred between polystyrene, SnCl_4 , and dichloroethane at 50°C .

Additional evidence of the structure was obtained by H^1 -n.m.r. analysis of selected samples in carbon tetrachloride. Figure 2 shows a typical n.m.r. spectrum, using trimethylsilane as a standard, and the assignment of associated peaks.

Water was excluded from the grafting reaction, since SnCl_4 can catalyse the reaction without cocatalyst.

Analysis of the reacting solution showed a relatively constant and minute amount of HCl dissolved in the solvent. Numerous references are cited by Olah¹, which indicate that the formation of a complex between HCl and SnCl_4 is not possible. A mechanism involving an alkyl halide- SnCl_4 complex is more likely. From this evidence, it was concluded that HCl was produced solely by the grafting-crosslinking reaction. The dissolved amounts of HCl were determined and taken in consideration when calculating the total amount of HCl evolved, and therefore, the total concentration of junctions formed.

The rate of reaction was determined by plotting the concentration of grafting points (junctions) as a function of time (Figures 3, 4 and 5). Sigmoid curves characterize all the kinetic data. The three sections of each S-shaped curve indicate an induction period, followed by a period of maximum reaction rate, and finally the onset of gelation accompanied by mass-transfer effects in the swollen network.

The maximum rate of grafting was obtained as the slope at the inflection point of the S-shaped junction concentration *versus* reaction time for each curve. The results of these maximum rates along with the initial concentration of DMDCB are presented in Table 4 for reactions in which the SnCl_4 concentration was held constant. The results of the maximum rates along with the initial concentration of SnCl_4 are presented in Table 5 for reactions in which the concentration of DMDCB was held constant.

The reaction was terminated after the onset of gelation. At this point, the reaction mixture transformed to a swollen gel-like material. The evolution of HCl was

Table 2 Reaction conditions and average molecular weights by cationic styrene polymerization*

Series	Reaction time (h)	Reaction temperature (°C)	[Styrene] (mol l ⁻¹)	\bar{M}_n	\bar{M}_w	Yield (%)
1	1	30	0.773	1800	3700	20.3
2	1	30	0.945	1950	4050	26.7
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* Catalyst [SnCl₄] = 0.020 ± 0.001 mol l⁻¹

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D	0.160	40	9600	180	0.0	0.05	0.14	0.65	2.57g	—	—
H	0.038	40	13000	480	0.0	—	0.03	0.14	0.33	1.09	2.50
E	0.159	50	11100	125	0.0	0.02	0.16	2.55	3.17g	—	—
G	0.038	50	10250	198	0.0	—	0.37	1.68	2.83	3.36g	—
F	0.158	60	9100	45	0.0	1.50	4.14g	—	—	—	—
J	0.038	60	11550	95	0.0	0.14	1.30	2.64g	3.56g	—	—
B	0.149	70	11200	30	0.0	3.82g	—	—	—	—	—
A	0.169	80	13600	25	0.0	6.95g	—	—	—	—	—

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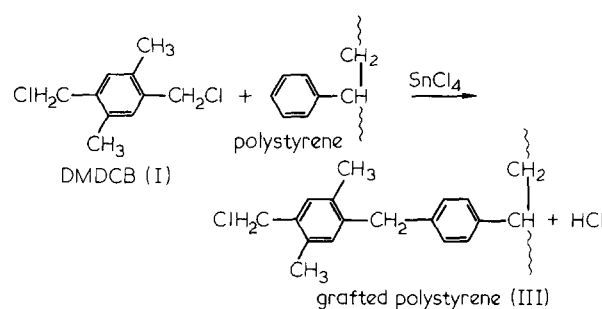
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The remaining chloromethyl group is free to react with either another molecule of DMDCB or another styrene unit of a polystyrene chain to give either of the polymer structures shown below:

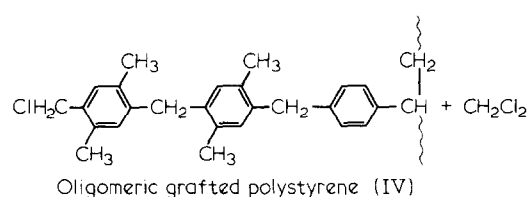


Table 6 Molar ratio of $[J]_t/[PS]_i$ as a function of reaction time

Series	L	M	O	P
$[DMDCB]_i$ (mol l ⁻¹)	0.038	0.071	0.147	0.283
$[PS]_i$ (mol l ⁻¹)	3.53	3.69	3.67	3.40
Reaction time (h)	$[J]_t/[PS]_i$ (mol/mol)			
0.25	—	3.8×10^{-5}	4.6×10^{-5}	—
0.50	3.7×10^{-5}	4.1×10^{-4}	3.5×10^{-4}	9.1×10^{-5}
0.75	8.9×10^{-5}	1.5×10^{-3}	5.7×10^{-4}	1.9×10^{-4}
1.00	1.7×10^{-4}	3.6×10^{-3}	9.2×10^{-4}	3.2×10^{-4}
1.25	4.1×10^{-4}	4.8×10^{-3}	1.5×10^{-3}	5.8×10^{-4}
1.50	1.6×10^{-3}	7.4×10^{-3}	2.8×10^{-3}	1.0×10^{-3}
1.75	3.3×10^{-3}	9.3×10^{-3}	4.9×10^{-3}	1.9×10^{-3}
2.00	5.1×10^{-3}	1.0×10^{-2}	7.7×10^{-3}	3.3×10^{-3}
2.25	6.9×10^{-3}	1.1×10^{-2}	9.4×10^{-3}	4.8×10^{-3}
2.50	8.1×10^{-3}	1.1×10^{-2}	1.0×10^{-2}	6.8×10^{-3}
2.75	—	1.1×10^{-2}	1.1×10^{-2}	1.0×10^{-2}
3.00	8.9×10^{-3}	1.1×10^{-2g}	1.3×10^{-2g}	1.4×10^{-2g}
3.25	—	—	—	1.8×10^{-2g}
3.50	9.4×10^{-3}	—	—	2.1×10^{-2g}
3.75	—	—	—	2.4×10^{-2g}
4.00	1.0×10^{-2g}	—	—	2.5×10^{-2g}

g = gel

$$j = \frac{[J]_t}{[PS]_i} \cdot r$$

Here $[J]_t$ is the concentration of junctions at time t , which can be obtained from the data of Figures 3, 4 and 5, $[PS]_i$ is the initial concentration of polystyrene as reported in Table 1, and r is the number of repeating units per initial polystyrene chain, which can be readily obtained from the M_n values reported in Tables 6 and 7. These tables summarize the effect of reaction time on the molar ratio $[J]_t/[PS]_i$, and on the number of junctions introduced, j , as a function of initial concentration of the crosslinking agent, $[DMDCB]_i$, for Friedel-Crafts grafting-crosslinking at 50°C with constant $[SnCl_4] = 0.020 \pm 0.001$ mol l⁻¹. Gelation is observed in all cases when the molar ratio $[J]_t/[PS]_i$ approaches values of 1.1 – 1.3×10^{-2} mol/mol, namely when there is one DMDCB molecule grafted for every 75–90 repeating units of polystyrene.

Ultraviolet spectroscopy can be used both as a qualitative and a quantitative tool for interpreting experimental work on crosslinking of polystyrene. Qualitatively, it is used to provide evidence of crosslinking while quantitatively it can be used to measure the degree of crosslinking as a function of time¹⁶. The u.v. spectra of both linear and grafted polystyrene are shown in Figure 1 for the wavelength range of 2500–3000 Å.

Evidence for crosslinking can clearly be seen by the absorption change at 2780 Å yielding a shoulder on the polystyrene peak. Not only does the shoulder at 2890 Å indicate grafting but it also indicates that the crosslinking monomer is bonded through the *p*-position with the polystyrene since the shoulder at 2780 Å is characteristic of 2,5-disubstituted *p*-xylenes. This desired linear bridge can be attributed to the presence of the methyl groups in the 1,4 positions of the crosslinking monomer which restrict the reaction to the *p*-2,5-dichloromethyl position.

The extent of reaction and degree of crosslinking can be determined by measurement of the optical density of the

sample at 2780 Å. The optical density at 2780 Å varies with the reaction time as shown in Figure 6. The plots are for DMDCB concentrations of 0.038 and 0.283 mol l⁻¹. As expected, increase in the concentration of DMDCB leads not only to an increase in rate but also to more extensive grafting which is reflected by the higher values of optical density.

CONCLUSIONS

Polystyrene may be grafted or crosslinked with 1,4-dimethyl-2,5-dichloromethylbenzene in dichloroethane at 50°C with SnCl₄ as the catalyst in a Friedel-Crafts

Table 7 Number of junctions per polystyrene chain as a function of reaction time

Series	L	M	O	P
$[DMDCB]_i$ (mol l ⁻¹)	0.038	0.071	0.147	0.283
$[PS]_i$ (mol l ⁻¹)	3.53	3.69	3.67	3.40
Initial \bar{M}_n	11 800	11 600	11 600	12 000
Polydispersity index	2.05	2.06	2.06	2.06
Reaction time (h)	Number of junctions per PS chain, j			
0.25	—	0.00	0.00	—
0.50	0.00	0.05	0.04	0.01
0.75	0.01	0.16	0.06	0.02
1.00	0.02	0.41	0.10	0.04
1.25	0.05	0.54	0.16	0.07
1.50	0.18	0.83	0.31	0.12
1.75	0.37	1.04	0.54	0.21
2.00	0.58	1.13	0.85	0.37
2.25	0.78	1.20	1.06	0.55
2.50	0.92	1.23	1.14	0.78
2.75	—	1.25	1.23	1.19
3.00	1.00	1.26g	1.34g	1.57g
3.25	—	—	—	2.09g
3.50	1.06	—	—	2.47g
3.75	—	—	—	2.74g
4.00	1.14g	—	—	2.86g

g = gel

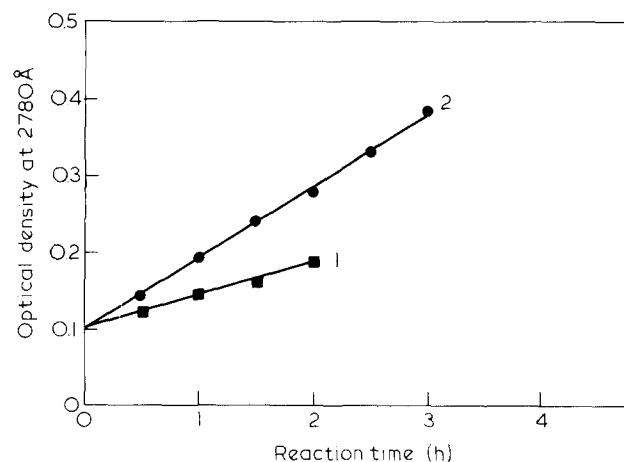


Figure 6 Optical density of grafted polystyrene at 2780 Å as a function of grafting reaction time and initial concentration of DMDCB. Line 1: $[DMDCB]_i = 0.038$ mol l⁻¹. Line 2: $[DMDCB]_i = 0.283$ mol l⁻¹

solution reaction. In comparison to the acidic catalysts, HClO_4 and H_2SO_4 , that were used previously¹⁰, SnCl_4 appears to be more reactive.

The extent of grafting may be followed up to the gelation point by determining the concentration of evolved HCl. Using values of the molecular weights of the initial polystyrene used, it is possible to calculate the number of junctions introduced in the grafted polystyrene.

Ultraviolet spectra of the grafted polymer give strong evidence of *p*-position linked DMDCB to polystyrene. Therefore, the crosslinked network may have more controlled structure than DVB-crosslinked systems, a very desirable feature in crosslinked polystyrene, which should yield favourable properties for chromatographic and ion-exchange resins.

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