Friedel-Crafts crosslinking methods for polystyrene modification:
2. T_g, T_{ll} and T'_{ll} transitions of grated polystyrene

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Polystyrene was grafted with 1,4-dimethyl-2,5-dichloromethyl benzene in dichloroethane solution at 50°C using $SnCl_4$ as a catalyst. Thermal analysis of grafted polystyrene samples using differential scanning calorimetry revealed two liquid–liquid transitions, T_{ll} *and* T'_{ll}, in addition to the glass transition, T_g, and the decomposition temperature, T_d. The effect of the number of junctions per polystyrene chain on T_g, T_{ll} and T'_{ll} is examined and analysed.

Keywords Branching; grafting of polystyrene; glass transition; liquid state transitions

INTRODUCTION

In the previous contribution of this series[1] experiments were discussed leading to the selection of a viable scheme for polymerization, grafting and crosslinking of polystyrene, based on Friedel-Crafts reactions of 1,4-dimethyl-2,5-dichloromethyl benzene (henceforth designated DMDCB) with polystyrene in dichloroethane solutions, using $SnCl_4$ as catalyst. Kinetics of the grafting reactions were presented and analysed, and mechanisms for these reactions were proposed.

Friedel-Crafts methods for grafting and crosslinking of polystyrene are based on reactions of chlorinated and chloromethylated derivatives of aromatic compounds such as benzene, *p*-xylene and durene with polystyrene, in solution using $AlCl_3$, $SnCl_4$, $ZnCl_2$, H_2SO_4, $HClO_4$, etc. as catalysts. The research of Grassie and his associates[2–4] and the early work of Peppas and his collaborators[5–7] concentrated on the investigation of the kinetics of these reactions, and the thermal properties of the polystyrene networks, especially as related to the increase of the glass transition temperature, T_g, as the crosslinking density of the network increased. The work of Davankov and his collaborators[8–19], Belfer and coworkers[20–23], as well as the most recent work of this research group[24–26] have also examined the physical nature of the crosslinks, the swelling behaviour of the Friedel-Crafts crosslinked networks, and the diffusive characteristics of the ensuing gels.

The ultimate objective of this and similar research on Friedel-Crafts crosslinking of polystyrene is the development of novel polystyrene gels for chromatographic and ion-exchange applications. Recently Peppas and Barar[24], and Regas and Papadoyannis[27] reported successful attempts to graft and crosslink polystyrene by Friedel Crafts methods in suspension, for the preparation of particles of controlled size distribution. In addition, several researchers have discussed the possible application of lightly crosslinked polystyrene networks as systems with increased thermal stability over polystyrene[4,7].

Grafted polystyrene is the precursor of crosslinked polystyrene networks of controlled structure. Only a limited number of studies are available on the thermal properties of grafted polystyrene[6,27]. The aim of the present work was to analyse observed transitions at or above the glass transition temperature at increasing degrees of grafting or increasing concentrations of junctions per polystyrene chain.

The results of this work can serve as additional evidence of T_{ll} and T'_{ll} liquid transitions, which have been observed by Boyer[28,29], Gillham[30–32] and other investigators[33,34] for anionically prepared monodisperse polystyrene, and which have been expertly analysed by Boyer[35–37] in recent reviews.

EXPERIMENTAL

Preparation and characterization of grafted polystyrene

The experimental techniques for Friedel-Crafts preparation of grafted polystyrene have been described in detail[1]. Briefly, grafting reactions of polystyrene were carried out in anhydrous, dichloroethane solutions containing DMDCB (prepared as reported previously[5,7]) as the grafting-crosslinking agent and $SnCl_4$ as the catalyst. The reaction temperature was kept at 50°C and the reaction kinetics were followed for 5 h or until gelation. The average initial concentrations of polystyrene and $SnCl_4$ in the reacting system were 3.62 ± 0.06 and 0.020 ± 0.001 mol l^{-1} respectively.

The polystyrene used in the grafting reaction was cationically prepared by reaction of styrene in dichloroethane in the presence of $SnCl_4$ as catalyst[1]. Molecular weight determination of the polystyrene samples before grafting was done by gel permeation chromatography (g.p.c.). G.p.c. runs were carried out at 3 ml min^{-1} with 20 μl samples of dilute polystyrene solutions in tetrahydrofuran, at $30° \pm 0.2$°C. The chromatography

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Table 1 Conditions of grafting reactions of polystyrene*

Series	[PS] (mol l^{-1})	[DMDCB] (mol l^{-1})	[$SnCl_4$] (mol l^{-1})	[DMDCB]$_i$/[PS]$_i$ (mol/mol x 10^2)	Initial polystyrene characteristics $\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
K	3.80	0.019	0.021	0.50	11 350	2.07
L	3.53	0.038	0.020	1.08	11 800	2.05
M	3.72	0.071	0.021	1.92	11 600	2.06
O	3.67	0.147	0.020	4.00	11 600	2.06
P	3.40	0.283	0.019	8.32	12 000	2.06

* All reactions were carried out in dichloroethane solution at 50°C

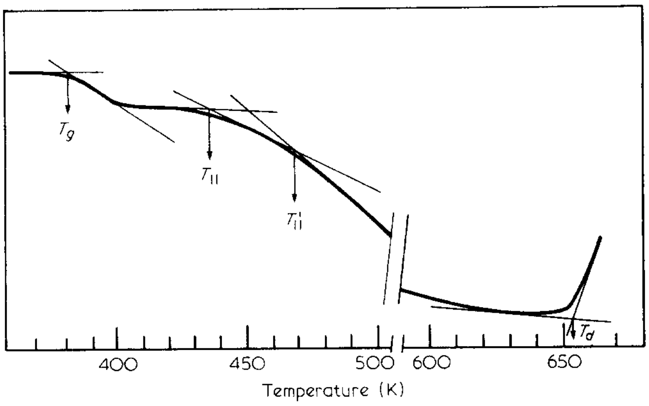


Figure 1 **D.s.c. thermogram of grafted polystyrene sample M120 showing method of determination of T_g (=380.5 K), T_{ll} (=432.5 K), T'_{ll} (=467 K) and T_d (=652 K)**

unit (model 6000 A, Waters Associates) was equipped with a refractive index detector, and five μ-Styrogel columns (2 $\times 10^2$, 10^3, 10^4, 10^5 Å nominal pore size) in series at 30° ±0.2°C. Calibration was done by conventional techniques using seven monodisperse polystyrene samples. A complete description of the experimental conditions for preparation of the polymers is given in *Table 1*. Techniques used for characterization of grafted polystyrene and for determination of the concentration of junctions were described in the previous contribution[1].

Upon completion of the grafting–crosslinking reaction all samples obtained at 30 min intervals and selected samples obtained after gelation had occurred were received, purified and dried as described before[1], and they were stored in dessicators under vacuum for 6 days.

Thermal analysis of grafted polystyrene

Thermal analysis of the previously prepared, purified and dried samples was done by differential scanning calorimetry (d.s.c.). In a typical experiment, an accurately weighed (±0.1 mg) quantity of grafted polystyrene (in the range of 8 to 12 mg) in the form of a thin film was placed in the appropriate pan, sealed and placed in one of the holders of a d.s.c. equipment (model DSC-2, Perkin Elmer, Norwalk, Conn.). In most experiments an empty pan and lid were used as the 'reference' sample. To investigate possible artifacts and deviations of the baseline slope due to weight differences between the polystyrene sample and the empty pan, as suggested by Boyer[36], the reference sample was prepared by employing a pan and three lids, while the polystyrene sample had only one lid.

Polystyrene samples were purged with dry nitrogen for 45 min and thermograms were obtained between 301 and 670 K at a scanning rate of 5 K min^{-1} at a full range of 4 mcal s^{-1}. Other scanning rates and ranges were also used for selected samples.

The thermograms obtained from these studies were analysed according to procedures developed by Enns *et al.*[38,39]. For example *Figure 1* shows the d.s.c. thermogram for grafted polystyrene sample M120. The glass transition temperature, T_g, was determined by the intersection of the baseline and the deflection of the curve, characteristic of the second order thermodynamic transition. The T_{ll} and T'_{ll} transitions were determined as the temperatures at the cross-section of the extrapolated tangents to the curve of the thermogram. The decomposition temperature, T_d, was determined as shown in *Figure 1*.

RESULTS

Thermograms of DMDCB-grafted polystyrene were analysed and four distinct transitions were observed, which were identified as the glass transition temperature, T_g, two liquid–liquid transitions, T_{ll} and T'_{ll}, and a decomposition temperature T_d.

The glassy amorphous state of polystyrene is more complex than originally supposed, and the molecular weight and grafting dependence of the relaxational behaviour on its macromolecular chains is not definitely known. Divisions have been suggested by Boyer[36,37] between the 'fixed' and 'true' liquid state, which correspond to relaxational regions that have been reported at temperatures between T_g and the decomposition temperature, T_d. These transitions can be classified as following:

(i) The glass transition temperature, T_g, involving segmental mobility, and usually observed at 370–380 K for linear, atactic polystyrene.

(ii) The liquid–liquid transition, T_{ll}, involving motion of the entire molecule, and usually observed at $T_{ll} = (1.20 \pm 0.05) T_g$ for polystyrene. Debate related to the true thermodynamic meaning of this transition has been amply discussed by Boyer[36,40].

(iii) A liquid–liquid transition, T'_{ll}, involving segmental mobility in the liquid state, and usually observed about 40 K above T_{ll} for several polymers.

(iv) A decomposition (degradation) temperature, T_d, usually observed at 560–620 K for polystyrene[4,30].

A grafted or crosslinked polystyrene may or may not exhibit all these transitions depending on the method of analysis, heating rate, sample history, degree of crosslinking and degree of crystallinity.

The peak temperatures at which these transitions were observed are reported in *Table 2* for all grafted polystyrene samples investigated. The same *Table* includes the number of junctions, *j*, of each grafted sample, which was calcu-

Table 2 Thermal analysis of grafted polystyrene samples

Sample	Junctions per PS chain, *j*	T_g (K)	T_{ll} (K)	T'_{ll} (K)	T_d (K)	T_{ll}/T_g
K0	0	370.5	427.5	449	–	1.15
K60	0.01	371	*	456	–	*
K120	0.04	371	428	462	622	1.15
K180	0.08	371.5	429	467	–	1.15
K240	0.12	372	430	467	627	1.15
K360	0.27	372.5	429	463.5	–	1.15
L0	0	370.5	426	*	–	1.15
L30	0.01	371	429	448.7	618	1.16
L60	0.02	371	428	*	–	1.15
L120	0.58	375.5	429.5	462	632	1.14
L180g	1.00	380	430.5	*	–	1.13
M0	0	370.5	429	453	612	1.16
M30	0.05	371.5	430	456.5	–	1.16
M60	0.40	374	430.5	458.5	–	1.15
M90	0.81	377.5	433	465	651	1.15
M120	1.10	380.5	432.5	467	652	1.14
M180g	1.22	381.5	430	471	653	1.13
O0	0	370	427	455	–	1.15
O30	0.04	370.5	427.5	*	–	1.15
O60	0.10	371.5	429	455	666	1.16
O90	0.31	372	429	442	–	1.15
O120	0.85	378	430.5	457	659	1.14
O180g	1.34	383	431	470	–	1.13
P0	0	369.5	426.5	*	–	1.15
P60	0.04	371.5	429.5	445	–	1.16
P120	0.37	373	430	448	614	1.15
P180	1.57	384	430.5	454	651	1.12

All samples were prepared as described in *Table 1*. The sample code used designates: letter = series of experiments, number = grafting reaction time in minutes. Samples followed by g are crosslinked networks. An asterisk (*) denotes non-detectable transitions. Some thermal analysis experiments were not run up to decomposition

lated as follows:

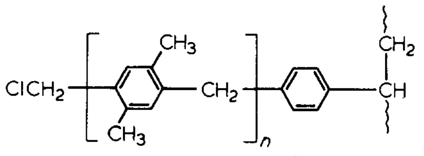
$$j = \frac{[\text{DMDCB}]_t}{[\text{PS}]_i} \times \frac{\bar{M}'_n}{M_r}$$

Here $[\text{DMDCB}]_t$ and $[\text{PS}]_i$ are the concentrations of DMDCB reacted and initial amount of polystyrene respectively (as reported before[1]), $\bar{M}'_n$ is the number average molecular weight of the initial polystyrene as determined by g.p.c. (see *Table 1*), and M_r is the molecular weight of the polystyrene repeating unit (= 104). Increasing values of the number of junctions, *j*, lead to increasing degree of grafting.

All data reported here are for scanning rate of $5\,\text{K}\,\text{min}^{-1}$ at a range of $4\,\text{mcal}\,\text{s}^{-1}$. Boyer and his collaborators[36–39] have discussed the importance of higher scanning rates (e.g. $10\text{–}40\,\text{K}\,\text{min}^{-1}$) when detecting T_{ll} and T'_{ll} transitions by d.s.c. In our studies a rate of $5\,\text{K}\,\text{min}^{-1}$ was used to minimize lag and tail-effects in the determination of the onset point of these transitions. Use of this slower scanning rate in no way impeded the clear identification of the associated transitions.

DISCUSSION

The importance of each transition observed, and the effect of increasing number of junctions, *j*, on transitions T_g, T_{ll}, T'_{ll} and on the decomposition temperature T_d are discussed here. It must be noted that, as shown before[1], the structure of DMDCB-grafted polystyrene (structure I) is characterized by $n = 1$.



Grafted polystyrene (I, n=1)

Before proceeding with the discussion of the thermal analysis results, a note on crystallinity is in order. Previous studies by Davankov *et al.*[10,19] and by our group[7] examined the crystallinity associated with the formation of Friedel-Crafts-grafted and crosslinked polystyrene. The degree of crystallinity is usually very low and it is associated mostly with long, linear bridging chains of the crosslinking agent, produced by the polycondensation reaction of DMDCB. In this study, only two grafted samples (L120 and M120) showed weak crystalline melting peaks, associated with melting temperatures, T_m, of 491 and 496 K respectively. The degree of crystallinity was found to be $X_t \leqslant 0.032$.

Glass transition temperature, T_g

The average glass transition temperature of cationically prepared polystyrene before grafting was determined as $\bar{T}_g = 370$ K (samples K0, L0, M0, O0, P0), which is somewhat higher than that reported[39] for anionically prepared polystyrene of similar $\bar{M}_n$. As the number of junctions per polystyrene chain, *j*, increases from 0. to 1.57, the glass transition temperature increases from 369.5 K to 383 K. This type of dependence of T_g on the degree of grafting is in qualitative agreement with the work of Boyer and his associates, if one considers that due to the low degree of grafting, the molecular weight of the polymer may be simply approaching its characteristic M_c value. The observed dependence of T_g on j is plotted in *Figure 2* for all samples tested.

Liquid–liquid transitions (T_{ll} *and* T'_{ll})

The two liquid–liquid transitions, T_{ll} and T'_{ll}, were observed for most samples, even in the presence of light crosslinking (samples L180, M180, O180). The T_{ll} transition increases slightly as the number of junctions increases. The ratio of T_{ll}/T_g varies in the range of 1.16 to 1.12, the lower limit of the relation proposed by Enns and Boyer[37,38], and it decreases slightly as the degree of grafting increases. The average value of T_{ll} for polydisperse polystyrene before grafting was $\bar{T}_{ll} = 427$ K, slightly higher than that reported by Enns and Boyer[38] for anionically prepared polystyrene of similar molecular weight.

Although the transition T'_{ll} was clearly observed in most samples under the experimental conditions employed, no general trend of the dependence of T'_{ll} on degree of grafting could be established. However, within the same set of preparation conditions, T'_{ll} increases as j increases.

Decomposition temperature (T_d)

The onset of decomposition is reported in *Table 2* as the decomosition temperature, T_d. The value of T_d increases considerably as the degree of grafting increases. This behaviour is observed at higher values of j, but always below gelation, and it is characteristic of thermal stability contributed to the polystyrene chains by the grafting agent and by the increase in chain entanglements as the grafting rection approaches gelation.

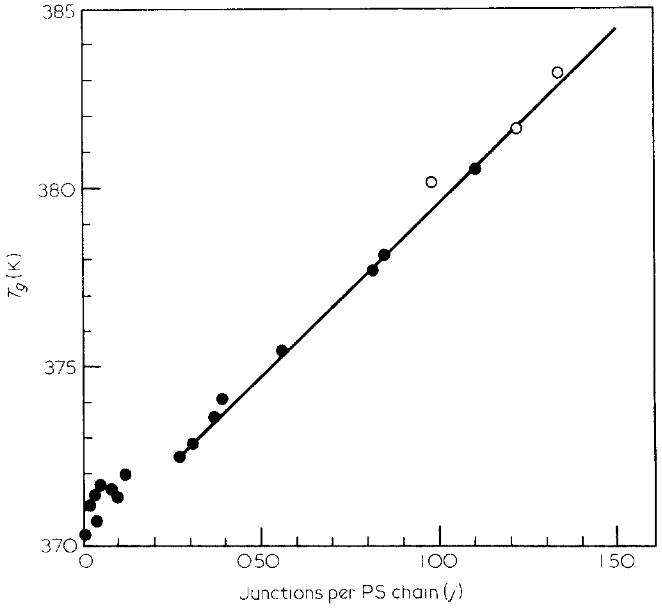


Figure 2 Glass transition temperature of grafted polystyrene, T_g, as a function of the number of junctions per polystyrene chain, j. The open circles are for lightly crosslinked samples, obtained near the gelation point

Transitions in crosslinked polystyrene samples

A selected number of crosslinked polystyrene samples was prepared by the same Friedel-Crafts technique described before (series P), and analysed by d.s.c. *Table 3* summarizes the various transitions observed.

Increase of the crosslinking density, as evident from the considerable increase of the number of junctions, j, per polystyrene chain, clearly impedes segmental mobility by increasing the glass transition, T_g (*Figure 3*). Similar behaviour has been observed before for Friedel-Crafts polystyrene networks crosslinked by various other grafting-crosslinking agents[4,6,7,25]. From the point of view of practical applications in the development of polystyrene with improved thermal stability and increased T_g, the polystyrene networks prepared registered some of the highest increase in T_g over the average value of the precursor polystyrene chains. *Table 4* summarizes values T_g determined by various investigators.

Another interesting result of the present study is that the increase of T_g with number of junctions per polystyrene chain does not seem to be linear for Friedel-Crafts crosslinked systems, as expected from the studies of Glans and Turner[41] for DVB-copolymerized/crosslinked polystyrene. The implication of this dependence may be related to the contribution of entanglements on T_g and is presently under investigation.

Of the two liquid–liquid transitions, T_{ll} vanishes at $j \approx 3.2$ and T'_{ll} becomes constant at approximately 467 K. Both observations are in agreement with previous studies by Enns and Boyer[39] for DVB-crosslinked polystyrene samples. No premelting phenomena or crystalline melting point, T_m, were observed with these polystyrene networks.

Finally, the degradation temperature increased up to 672 K, which is in general agreement with previous studies by Grassie *et al.*[4].

CONCLUSIONS

Polystyrene samples obtained during the grafting reaction of linear polystyrene with DMDCB under Friedel-Crafts reaction conditions were analysed by differential scanning calorimetry to determine their transition and decomposition temperature. The glass transition temperature increases as the degree of grafting and crosslinking, and it approaches a constant value at about 6 junctions per polystyrene chain.

Table 3 Thermal analysis of crosslinked polystyrene

Sample	Junctions per PS chain, j	T_g (K)	T_{ll} (K)	T'_{ll} (K)	T_d (K)	T_{ll}/T_g
P240	2.80	389	432	457	654.5	1.11
P255	2.90	389.5	432	462	657	1.11
P270	3.05	391	433	463	659	1.11
P285	3.18	393	434	464.5	665	1.11
P300	3.25	393	*	464.5	–	*
P330	3.47	395	*	467.5	–	*
P360	4.16	396	*	465	672	*
P420	4.82	397	*	467.5	670	*
P540	6.15	397	*	*	–	*

* Not observed. For explanation of sample code see *Table 2*

Table 4 Maximum increase of glass transition of polystyrene upon Friedel-Crafts crosslinking

Crosslinking agent	Crystallinity	Maximum ΔT_g over linear polystyrene	Method of analysis	Reference
dichloromethyl benzene	unknown	14.0	d.t.a.	4
2,5-dimethyl benzylchloride	observed	12.5	d.s.c.	6, 7
1,4-dichloromethyl-durene	observed	3.5	d.s.c.	6, 7
DMDCB* (50°C)	not observed	23.0	d.s.c.	this study
DMDCB* (80°C)	observed	51.0	d.s.c.	25
DMDCB** (100°C)	observed	17.5	d.s.c.	7
oligo-methyl benzylenes	observed	4.8	d.s.c.	6,7

* Catalyst $SnCl_4$, solvent dichloroethane
** Catalyst $HClO_4$, various solvents

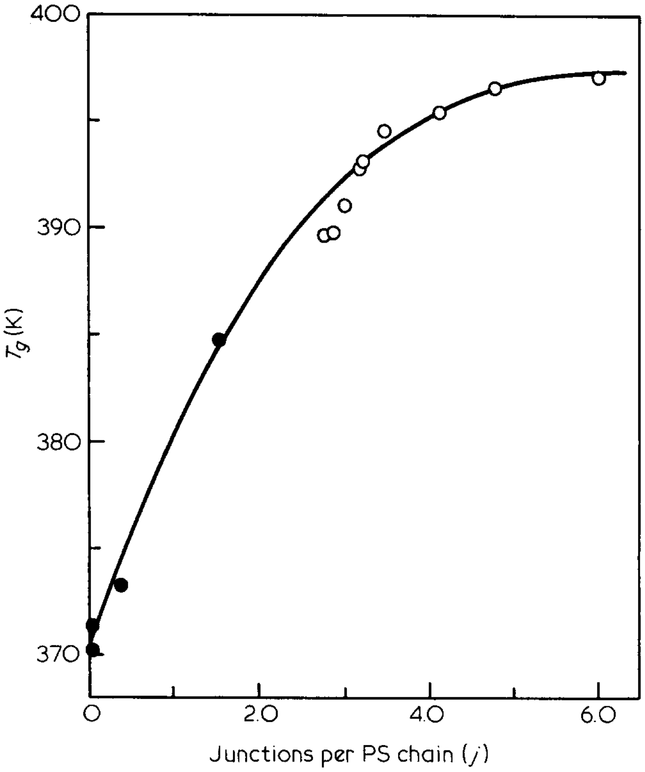


Figure 3 Glass transition temperature of grafted (●) and crosslinked (○) polystyrene as a function of the number of junctions per polystyrene chain. All samples prepared at same conditions (series P)

Two liquid–liquid transitions, T_{ll} and T'_{ll}, were also detected for most of the samples tested. The value of T_{ll} passes through a maximum as the degree of grafting increases to a level where gelation and further crosslinking occurs. However, T'_{ll} generally increases as the degree of grafting increases.

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