

## A New Method To Generate Polystyrene Gels

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### Introduction

Gels made of cross-linked polystyrene have been prepared and investigated since the dawn of polymer science.<sup>1,2</sup> Besides network formation by cross-linking copolymerization of the monomer with a suitable multifunctional cross-linker, random or directed successive cross-linking of preformed linear polymers has been used widely to generate networks in a more controlled manner. It is expected that networks made by successive cross-linking of preformed polymers are more homogeneous than those synthesized via cross-linking copolymerization.<sup>3</sup>

Unfunctionalized PS has been cross-linked making use of the electrophilic aromatic substitution reaction with *p*-xylylene dichloride<sup>4–6</sup> or chlorodimethyl ether<sup>4</sup> in the presence of Lewis acids. Randomly functionalized PS like poly(styrene-*co*-aminomethylstyrene), P(S-*co*-AMS), could be cross-linked by reaction with terephthaldialdehyde.<sup>7,8</sup> So-called model networks have been made by end-linking of telechelic precursors.<sup>9,10</sup>

Contrary to purely chemical reactions, photochemical cross-linking provides the opportunity of controlling the rate and the extent of the reaction at will, simultaneously offering potential for spatial differentiation. Photochemical cross-linking has been applied to a number of polymers where the linear precursors carried anthracene, cinnamate, indene, dimethylmaleimide, or coumarin moieties.<sup>11–22</sup> Most of these groups are bulky, and it is unclear how much they influence the properties of the polymer. In this paper, we will show that PS carrying a small number of mere aminomethyl groups can be photo-cross-linked in an easy and straightforward way. The aminomethyl moieties in *p*-position dimerize upon irradiation in the presence of thioxanthone (TX), thus forming benzylidenebenzylamine linkages. Starting from functionalized PSs of different molecular weights, the gelation process was followed by oscillatory shear measurements. Static light scattering was applied to obtain some structural information on the networks in addition to the macroscopic properties obtained by rheology.

### Experimental Section

Linear polystyrenes having molecular weights in a range from 123 000–900 000 g/mol and polydispersities  $M_w/M_n < 1.1$  were purchased from Pressure Chemical Co, Pittsburgh, PA. A polydisperse PS with  $M_n = 168\,000$  g/mol and  $M_w = 370\,000$  g/mol was obtained from BASF, Germany. By a two-step polymer analogous reaction, these polymers were converted into P(S-*co*-AMS) carrying 0.3–0.5 mol % aminomethyl moieties.<sup>8,23</sup> The degree of functionalization was kept very low to ensure that the PS properties were not affected significantly.

Cross-linking of the P(S-*co*-AMS)s in semidilute solution in toluene was performed by irradiation with UV light ( $\lambda = 370 \pm 18$  nm, 100 W Xe arc lamp equipped with band-pass filter) in the presence of TX as a photoinitiator. Each sample was irradiated at

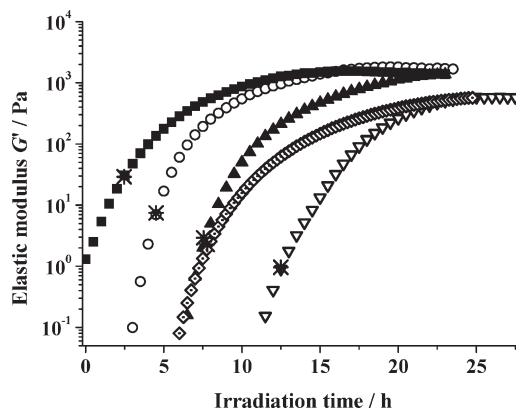
least 24 h to ensure completion of the reaction. The concentration of the copolymers ranged between 75 and 200 g/L, and the concentration of TX was adjusted so that only 10% of the incident light was absorbed by the sample to avoid formation of a gradient. The corresponding layer thickness was 1 mm for rheological measurements ( $c_{TX} = 14$  mg/L) and 1 cm for static light scattering ( $c_{TX} = 1.4$  mg/L).

The gelation process was followed by oscillatory shear experiments on a rheometer (Gemini, Malvern/Bohlin Instruments GmbH) equipped with a quartz glass plate which allows for irradiation of the sample from the bottom during the rheological measurements. A shear frequency of 1 Hz and a stress amplitude of 0.5–1 Pa were chosen. A solvent trap was used to avoid solvent evaporation during the rheological experiments.

Static light scattering measurements were mostly performed on a Fica SLS instrument. Only for measurements of the position-dependent scattering, an ALV/CGS-3 compact goniometer (ALV, Langen, Germany) was employed because of the smaller scattering volume. The light source on both instruments was a He–Ne laser operating at a wavelength of 633 nm. The measuring temperature was 25 °C. Scattering intensities were monitored in the range from 30° to 145° in steps of 5°.

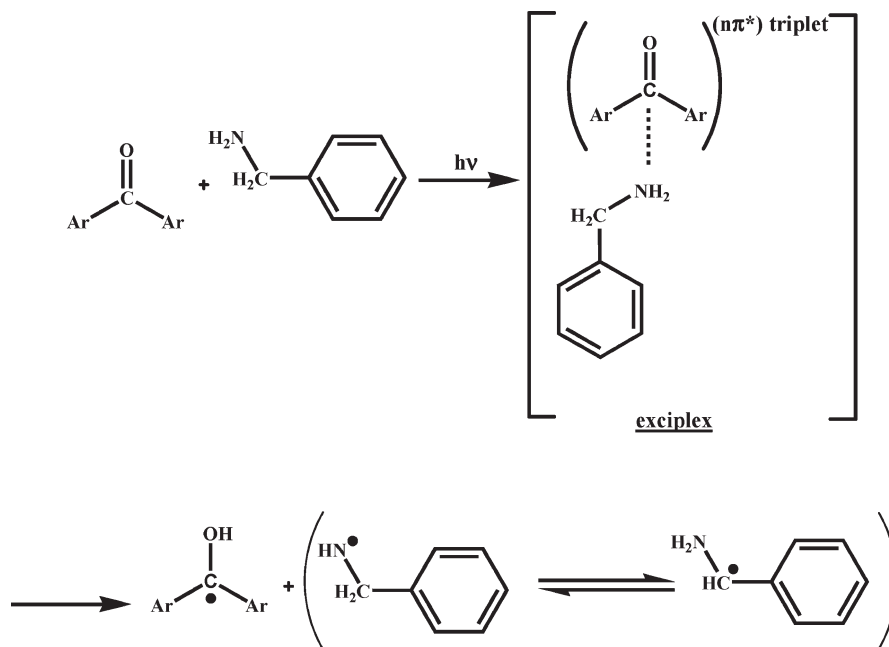
### Results and Discussion

Figure 1 shows the increase of the storage modulus,  $G'$  (1 Hz), during irradiation of solutions in toluene of polystyrenes carrying around 0.4–0.5 mol % of *p*-aminomethyl moieties. Polymers having different molecular weights are compared at a concentration of 100 g L<sup>-1</sup>, while the concentration of thioxanthone is 0.065 mmol L<sup>-1</sup>. This corresponds to roughly 60–80 amino groups per TX molecule. The loss modulus,  $G''$ , rises simultaneously, but far less than the storage modulus (not shown). The asterisks in Figure 1 indicate where the  $G'(t)$  and  $G''(t)$  curves



**Figure 1.** Elastic modulus  $G'$  (1 Hz) as a function of irradiation time (progress of photo-cross-linking) for five different polymers with similar degree of functionalization,  $c = 100$  g/L. Molecular weight:  $\nabla$ , 123 000 g/mol;  $\blacktriangle$ , 200 000 g/mol;  $\circ$ , 390 000 g/mol;  $\blacksquare$ , 900 000 g/mol;  $\diamond$ , 370 000 g/mol (broad). Asterisks indicate  $G' = G''$  ( $\approx$  gelation threshold).

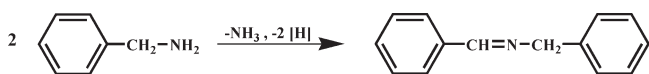
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Scheme 1. Radical Formation by H-Abstraction from Benzylamine by Excited Diaryl Ketone in Its  $n\pi^*$  Triplet State

intersect, thus serving as an approximate measure of the gelation threshold.

The strong initial rise of the storage modulus, after an induction period that is prolonged when the molecular weight of the starting polymer decreases, and its subsequent approach of a plateau value,  $G'_\infty$ , are indicative of the gelation process. Before analyzing the  $G'(t)$  curves in any depth, we will turn to a discussion of the underlying cross-linking mechanism.

Model experiments were performed by irradiating benzylamine (20 mmol/L in toluene) in the presence of 0.2 mmol/L TX for 1 week, thus mimicking the actual reaction conditions. The NMR analysis of the product provided clear evidence for *N*-benzylidenebenzylamine plus a small amount of unreacted educt ( $\text{C}_6\text{H}_5\text{-CH}_2\text{N=CH-C}_6\text{H}_5$ ;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 4.82$  (s, 2H,  $\text{N-CH}_2$ ), 7.23–7.42 (m, 8H), 7.75–7.79 (m, 2H), 8.38 ppm (s, 1H,  $\text{N=CH}$ ). These experiments prove that the dimerization of the *p*-aminomethyl moieties according to



is the relevant reaction. According to literature, this reaction leading to cross-linking in the actual system proceeds via a radical mechanism.<sup>24</sup> By absorption of a photon, TX is raised to an excited singlet state, and this process is immediately followed by intersystem crossing to a relatively stable  $n\pi^*$  triplet state. Since this is an electrophilic state, an exciplex is formed with an aminomethyl group followed by an electron and a proton transfer from the amine to the excited TX, thus generating radicals (Scheme 1).<sup>25–27</sup>

Ohkubo et al. suggested that hydrogen abstraction from the benzyl form of the radical leads to benzylideneamine, which then reacts with benzylamine to give *N*-benzylidenebenzylamine.<sup>24</sup> Oxygen, which is present in solution at ample concentration ( $\approx 2$  mmol/L)<sup>28</sup> unless particular precautions are taken for its exclusion, acts as a scavenger for the hydrogen and is also involved in bringing the TX back to its ground state.<sup>25</sup>

The first steps in this mechanism are identical to the widely used initiation of a radical polymerization by the amine–ene reaction.<sup>26,27,29</sup> This reaction is often initiated by diaryl ketones like benzophenone or by camphorquinone.<sup>26,30,31</sup> We use TX

because of its absorption band at higher wavelengths. It must be noted that TX is often employed as a photosensitizer because it assumes a  $\pi\pi^*$  triplet state as the lowest triplet state in protic solvents. In contrast, the  $n\pi^*$  state is the lowest triplet state in aprotic solvents, and this one is prone to initiate radical reactions if suitable hydrogen donors are present.<sup>32,33</sup>

The function of oxygen as a hydrogen scavenger was verified by repeating some of the model experiments carefully excluding oxygen by repeated freeze–pump–thaw cycles. Under such conditions, no or very limited dimerization of benzylamine was observed.

In view of this mechanism, the  $G'(t)$  curves shown in Figure 1 can be discussed in more detail. The light intensity used for the cross-linking experiments in the rheometer ( $30 \mu\text{W}/\text{cm}^2$ ) amounts to  $10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$  of absorbed photons. Assuming as an upper bound a quantum yield of 1, this results in just the same concentration of cross-links generated per second. The gelation threshold of one cross-link per chain would then be reached after 15 min of irradiation for the precursor having  $M_w = 900\,000$  g/mol and after 2 h for the precursor having  $M_w = 123\,000$  g/mol. The actual gelation times are longer (the gelation threshold was reached after 2.4 h (900 000 g/mol), 4.5 h (390 000 g/mol), 7.6 h (200 000 g/mol), and 12.5 h (123 000 g/mol), respectively), but considering that the quantum yield may be smaller than 1 and that cross-links are wasted by intramolecular linkages, the agreement within an order of magnitude between estimated and experimentally observed gelation times is remarkably good and consistent with the mechanism described above.

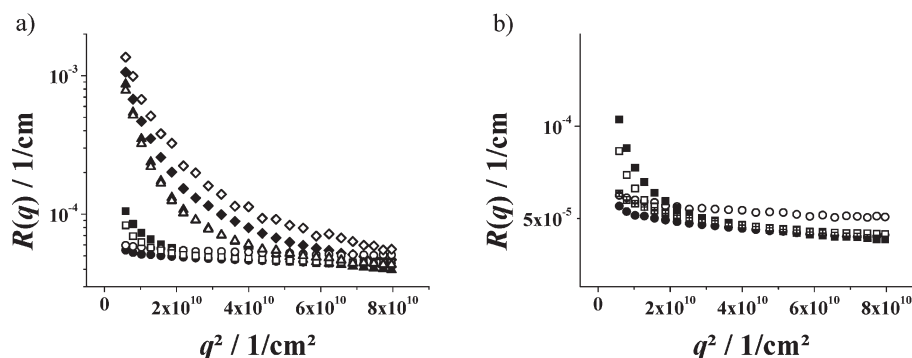
The final shear modulus,  $G'_\infty$ , is a useful quantity for the macroscopic characterization of the formed gels. It is a measure of the network density,  $\nu_{\text{eff}}$ , i.e., the number of effectively elastic network strands per volume, or the average molecular weight of the effective network chains,  $M_c$ . According to the theory of phantom networks, which is applicable to highly swollen gels,  $\nu_{\text{eff}}$  and  $M_c$  are obtained by eq 1:<sup>34</sup>

$$\nu_{\text{eff}} = \frac{c}{M_c} = \frac{G'_\infty}{RT \left( \frac{f-2}{f} \right)} \quad (1)$$

where  $f$  is the functionality of the junction points ( $f = 4$  for our systems),  $c$  is the concentration of the network polymer in the gel,

**Table 1. Characteristic Network Parameters Estimated from the Rheological Measurements of Gels Made of P(S-co-AMS) with Different Molecular Weights and at Different Concentrations**

$M_w$ /g/mol	concn $c$ /g/L	overlap concn $c^*$ /g/L	deg of functionaliza- tion/mol %	$G'_{\infty}$ /Pa	$\nu_{\text{eff}}$ /mol/m <sup>3</sup>	$M_c$ /g/mol	cross-linking efficiency/%
123 000	100	24.7	0.56	583	0.47	210 000	8.9
200 000	100	16.9	0.51	1380	1.11	90 000	22.7
390 000	100	10.0	0.37	1820	1.47	68 000	41.0
900 000	100	5.2	0.38	1550	1.25	80 000	34.5
370 000 (broad)	100	10.4	0.45	568	0.46	220 000	10.7
390 000	75	10.0	0.34	997	0.80	120 000	32.5
390 000	100	10.0	0.34	1540	1.24	80 000	37.7
390 000	200	10.0	0.34	3420	2.76	35 000	41.8

**Figure 2.** (a) Scattering intensities of 390 000 g/mol P(S-co-AMS), 0.34 mol % functionalized, at different concentrations in the sol state (filled symbols) and in the gel state (open symbols): (●, ○)  $c = 75$  g/L, (■, □)  $c = 100$  g/L, (▲, △)  $c = 150$  g/L, (◆, ◇)  $c = 200$  g/L. (b) blow-up of (a) also including data for pristine PS at 100 g/L (□).

$T$  is the temperature, and  $R$  is the gas constant. Table 1 contains a listing of the characteristic network parameters calculated from the rheological data. By taking the ratio of  $\nu_{\text{eff}}$  and the corresponding quantity calculated on the assumption that one cross-link is formed per two aminomethyl groups present, the cross-linking efficiency shown in the last column of Table 1 is calculated.

The cross-linking efficiency is in most cases around 30–40%, significantly higher than the cross-linking efficiency typically observed for cross-linking copolymerizations. Only when the molecular weight of the starting material is rather low or when a polydisperse starting material is used does the cross-linking efficiency drop down to ~10%. This is so because a fairly large amount of chain ends exists in such networks. Furthermore, the fact that the effective molecular weight between cross-links,  $M_c$ , then becomes larger than the molecular weight of the starting material is indicative of imperfect network structures. On the other hand, when one starts from molecular weights above 200 000 g/mol, high cross-linking efficiencies are observed, and one can assume rather perfect and homogeneous networks.

Under a different point of view, the actual concentration has to be appreciably larger than the overlap concentration  $c^*$  (listed in Table 1 in column 3) to result in high cross-linking efficiency. For the 390 000 g/mol sample, gelation was achieved at a concentration as low as  $30 \text{ g/L} \approx 3c^*$ .

Static light scattering provides a possibility to analyze spatial network inhomogeneities that are typically found on length scales in the range of 10–100 nm.<sup>8,35–38</sup> The scattering of polymer gels originates from thermal concentration fluctuations equivalent to those observed in solution and from permanent concentration fluctuations fixed by the chemical cross-links. The latter contribution is known as excess scattering and can be used to analyze the topological structure of gels.<sup>39,40</sup>

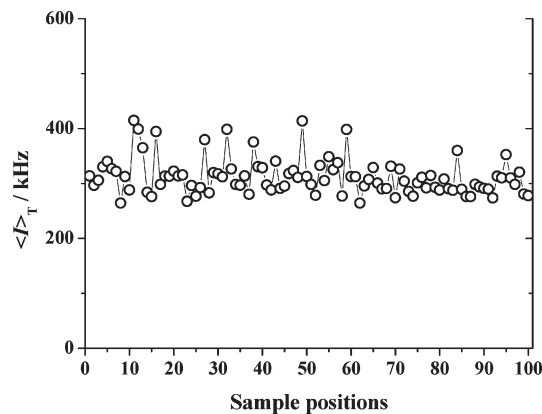
In our experiments, we measured the scattering intensity as a function of the scattering angle in the solution and in the fully cross-linked gel using the P(S-co-AMS) with  $M_w = 390\,000$  g/mol at four different concentrations. Measurements were taken with

a large scattering volume to obtain ensemble averages. Results are shown in Figure 2, with Figure 2b being a blow-up for a better display of the low concentration data. For comparison, the scattering curve of a solution of the corresponding unmodified PS at 100 g/L is also included.

At 75 and 100 g/L, the scattering curves are rather flat, except for an upturn at low  $q$ , and the scattering of the sol and the corresponding gel are virtually identical. Minor differences are due to experimental uncertainty, as expressed by the fact that in one case the solution scattering seems to exceed the gel scattering, and can be neglected. (Note that the usual excess scattering observed in gels made by cross-linking copolymerization amounts to a multiple of the solution scattering.) There is also no perceptible difference between the scattering of the solution of the unmodified and the functionalized PS. At 150 and 200 g/L, a considerable  $q$ -dependence is observed, but again there is no significant difference between sol and gel scattering. Such  $q$ -dependence also appears in concentrated solutions of unmodified PS; its origin is still subject to debate.<sup>41</sup> We can conclude, therefore, that the photochemical cross-linking of P(S-co-AMS) leads to gels without a perceptible extent of network inhomogeneities.

When the degree of functionalization of the PS is increased to ~1 mol % (data not shown), the scattering intensities of the solution and of the corresponding gel are markedly higher than at the low degrees of aminomethylation employed throughout this paper. This can be understood as a consequence of the incompatibility between the rather polar amino functionalities and the nonpolar environment. However, even in this case, the gelation does not lead to a further enhancement of scattering intensity. At degrees of functionalization below 0.5%, thermodynamic properties seem not to be affected.

Using a small scattering volume, the dependence of the time-averaged scattering intensity  $\langle I \rangle_T$  on sample position was studied. Figure 3 shows results obtained on a gel formed by photo-cross-linking of P(S-co-AMS) with molecular weight  $M_w = 390\,000$  g/mol. Only slight fluctuations of  $\langle I \rangle_T$  (measured as photon



**Figure 3.** Position dependence of time-averaged scattering intensity  $\langle I \rangle_T$  of P(S-co-AMS) with  $M_w = 390\,000$  g/mol (degree of functionalization: 0.31 mol %) in the gel state after 24 h of irradiation;  $c = 100$  g/L, scattering angle =  $90^\circ$ .

counts per second) around the ensemble average  $\langle I \rangle_E \approx 310$  kHz can be observed, and they are significantly smaller than those determined for gels made by cross-linking copolymerization.<sup>36,42</sup> The fluctuating component of the scattering intensity  $\langle I_F \rangle_T$  arising from dynamic, liquidlike concentration fluctuations was determined by the Joosten method.<sup>43</sup> For the experiment shown in Figure 3,  $\langle I_F \rangle_T \approx 290$  kHz. Hence, the ensemble-averaged scattering intensity  $\langle I \rangle_E$  is only slightly higher than  $\langle I_F \rangle_T$ .

Similar findings were reported for PMMA gels made by another photo-cross-linking reaction,<sup>44</sup> substantiating the fact that the subsequent cross-linking of existing macromolecules leads to more homogeneous network structures than cross-linking copolymerization.

## Conclusions

PS gels can be prepared in a convenient, efficient, and controlled way by irradiating a semidilute solution of PS carrying a few aminomethyl moieties in the *p*-position. In the presence of a suitable photoinitiator, such groups dimerize, thus forming linkages of the benzylidenebenzylamine type between different PS chains. Modulus measurements prove that the gels are formed with fairly high cross-linking efficiency. They also seem to be rather homogeneous as indicated by static light scattering.

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