

# Aminosilane Grafting of Plasticized Poly(vinyl chloride) II. Grafting and Crosslinking Reactions

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**ABSTRACT:** The reaction of poly(vinyl chloride) (PVC) in a plasticized formulation, with *N*-(2-amino ethyl)-3-aminopropyl trimethoxy silane yielded silane-grafted PVC that was crosslinked by a hydrolytic mechanism. The grafting of the aminosilane was carried out during processing on a two-roll mill, followed by compression molding. The grafting and crosslinking reactions were followed by measuring the gel content and by observing the changes in concentration of different structures using Fourier transform infrared (FTIR). Syndiotactic structures in the PVC seemed to be more reactive than isotactic structures with respect to crosslinking. The changes in molecular weight distribution before and after crosslinking were also followed using gel permeation chromatography (GPC); increases in both  $M_w$  and  $M_n$  were found and were attributed to chain extension reactions. After crosslinking, the remaining soluble polymer was found to have a low molecular weight. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2121–2128, 1997

**Key words:** PVC; crosslinking; grafting; aminosilane

## INTRODUCTION

Chemical crosslinking of plasticized poly(vinyl chloride) (PVC) offers a number of advantages in terms of their subsequent properties, in particular, their mechanical properties at elevated temperature. Various silane compounds have been used for this purpose.<sup>1–9</sup> In a previous article,<sup>10</sup> the effects of crosslinking conditions on the rate and extent of crosslinking have been studied for a plasticized PVC compound containing an aminosilane as crosslinking agent. In this work, grafting and crosslinking reactions are studied in more detail.

In a recent article, Hjertberg et al.<sup>11</sup> discuss the effect of certain catalysts on the rate of crosslink-

ing of PVC with dithioltriazines and also the changes in molecular weight distribution before crosslinking. Gel permeation chromatography (GPC) showed an extensive molecular enlargement before crosslinking. Large changes in molecular weight distribution for a sample crosslinked with catalyst were observed;  $M_w$  increased from  $1.2 \times 10^5$  in the virgin polymer to  $5.3 \times 10^5$  after 15 minutes in a roll mill at 145°C. The sample without catalyst also showed an increase in  $M_w$  up to  $1.9 \times 10^5$ .

The use of spectroscopic techniques for the analysis of polymer networks has received little attention in the literature.<sup>12</sup> Nevertheless, some approaches to such investigation have been reported. Frank<sup>13</sup> used infrared (IR) spectroscopy to investigate the radiation crosslinking of polyethylene. Nakamura and Mori<sup>14</sup> utilized IR spectroscopy to characterize the gel formed after crosslinking PVC with dithiols. Silane-modified polyethylene has been characterized using IR

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spectroscopy. Bullen et al.<sup>15</sup> followed the crosslinking formation, Si—O—Si, through a band that appeared at 1025 cm<sup>-1</sup>. They also observed the formation of a silanol band at 3690 cm<sup>-1</sup> after the hydrolysis of the methoxy group.

Hjertberg et al.<sup>16</sup> studied the crosslinking reaction of an ethylene vinyltrimethoxy silane copolymer. The kinetics were followed by determination of the content of different structures (Si—OCH<sub>3</sub>, Si—OH, and Si—O—Si) using FTIR. It was stated that the structures gave characteristic peak absorbances as follows: Si—OCH<sub>3</sub>, 800, 1090 cm<sup>-1</sup><sup>17,18</sup>; Si—OH free, 3691 cm<sup>-1</sup><sup>18</sup>; Si—OH hydrogen bonded, 3549, 3431 cm<sup>-1</sup><sup>19</sup>; Si—O—Si, 1030 cm<sup>-1</sup>.<sup>17,18</sup> The authors pointed out that it was difficult to quantify the Si—O—Si since it appears as a shoulder on the large band due to the Si—O band in Si—OCH<sub>3</sub>.

Kumar et al.<sup>20</sup> studied the graft copolymerization of vinylsilanes on to polyethylene during reactive processing; the graft copolymer was characterized by IR spectroscopy using the absorbance band at 1090 cm<sup>-1</sup>. Palmlöf et al.<sup>21</sup> studied the crosslinking of ethylene vinylsilane copolymers. The crosslinking reaction was followed by determination of the gel content and by analyzing the structural changes using FTIR; they used the band at 1030 cm<sup>-1</sup> characteristic of the Si—O—Si bond. The overall reaction was also followed quantitatively by GPC analysis of the soluble fraction.

The aim of this work described here was to investigate the grafting and crosslinking reactions of PVC grafted with 3(2-amino-ethylamino)propyltrimethoxysilane. The grafting occurs during processing, and the crosslinking by immersion in water. In the presence of moisture and a condensation catalyst, the alkoxy group of the silane derivatives pendant to the grafted PVC converts to a silanol group and undergoes a condensation reaction to form —Si—O—Si— type network. Both the hydrolysis of alkoxy silanes to silanol and their condensation reaction occur almost instantaneously. The grafting and crosslinking were followed using FTIR. Some molecular enlargement occurred during the grafting process, so a detailed study was carried out to investigate the effect of processing, and crosslinking agent concentration on molecular weight. The crosslink density of the gel was also evaluated.

## EXPERIMENTAL

### Materials

Materials used were as follows. Suspension poly(vinyl chloride) (PVC Corvic S71/102), with a K

value of 71 was supplied by ICI Ltd., U.K.; di-2-ethyl hexyl phthalate (DOP) was used as plasticizer; dibutyltinthioglycolate ester (T192), heat stabilizer, and dibutyltin dilaurate (TL) catalyst, were supplied by Akros Chemicals; the crosslinking agent was *N*-(2-aminoethyl)-3-aminopropyltrimethoxy silane, (Z-6020) supplied by Dow Corning, UK.

### Preparation

The formulation used contained 100 phr PVC, 50 phr of DOP, 2 phr of T192 heat stabilizer, and 3 phr of aminosilane (in which phr is parts per hundred of resin). The compounds were dry blended in a Henschel intensive mixer. The resin was preheated to 90°C, after which the plasticizer and the other ingredients were added. A total mixing time of 20 minutes was chosen in order to achieve good mixing.

Dry blends were roll milled at 145°C for different times, from 1 to 10 minutes. The milled sheets were then pressed for times from 2 to 10 minutes at 180°C.

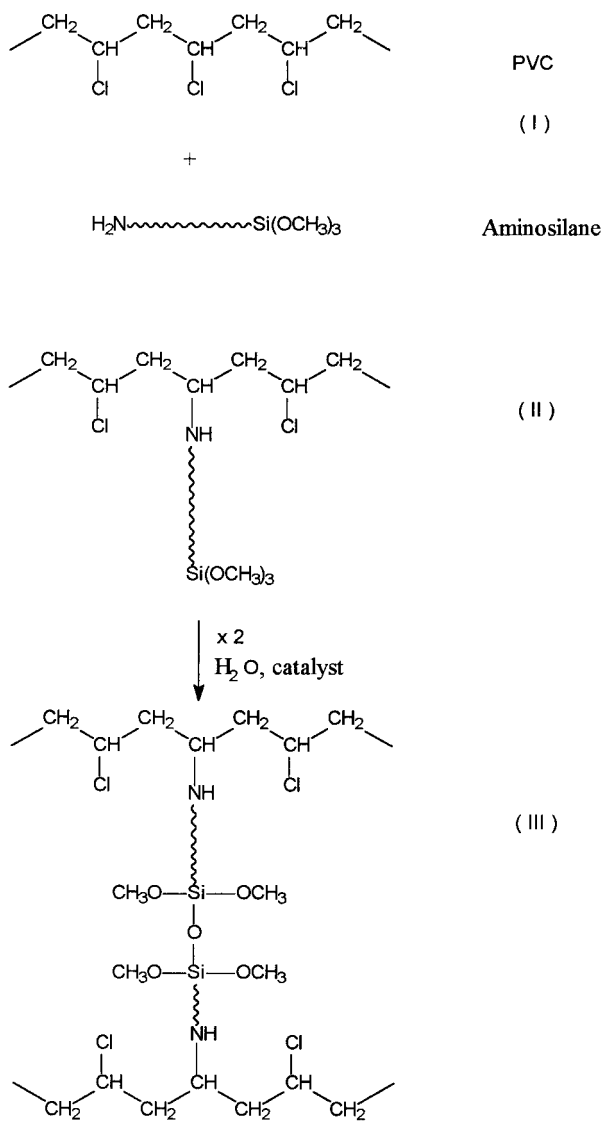
### Crosslinking Process

The crosslinking of the grafted PVC was carried out in steam at 120°C.

### Characterization of Grafted and Crosslinked Structures

To elucidate how the aminosilane is grafted onto the PVC molecule, it was necessary to extract the plasticizer and eliminate any unreacted aminosilane present. After Soxhlet extraction with diethyl ether, the soluble fraction was precipitated with methanol, then dissolved and then reprecipitated until all the unreacted aminosilane was eliminated. FTIR analysis shows that after three precipitations, the aminosilane and plasticizer were completely removed.

To follow the grafting and crosslinking reactions, i.e., changes in amounts of structures I–III (Scheme 1), the absorption frequencies given in Table I were used. The insoluble gel was swollen in THF; and after three days, the swollen gel was deposited in a glass slide, the solvent was evaporated under an infrared lamp, and the infrared spectrum was obtained.



Scheme 1

### Crosslink Density

The number-average molecular weight between crosslinks ( $M_c$ ) was determined using the Flory Rehner equation,<sup>22</sup> with the determination being made on the gel after removal of soluble material. The samples were swollen in methyl ethyl ketone for seven days at room temperature. The swollen and deswollen weights were used to calculate the volume fraction of PVC in the network swollen to equilibrium.

## RESULTS AND DISCUSSION

### Spectroscopy Analysis

Figure 1 shows the IR spectrum of normal PVC. Its characteristic bands have been assigned by

Krimm et al.<sup>23-24</sup> Figure 2 is the IR spectrum of the swollen gel. This spectrum shows some differences when compared with that of the pure PVC: a broad band at 3325 cm<sup>-1</sup>, a small band at 1662 cm<sup>-1</sup>, and two small shoulders in the region between 1100 and 1020 cm<sup>-1</sup>. The first band could be associated with the N—H stretching of the grafted aminosilane or the O—H stretching of the hydrolysed methoxy group of the aminosilane, although it is more probable that is associated with hydrogen-bonded silanols, as indicated by Smith.<sup>17,18</sup> The second band could be due to unsaturation introduced during the grafting process (it is known that during substitution reactions, some elimination also takes place producing unsaturation), and the third bands could be associated with the formation of siloxane bonds (Si—O—Si) during crosslinking.

The IR spectra of the gel and recovered soluble fraction are shown in Figure 3. It can be seen that the gel spectrum has several bands in the region of 1660 cm<sup>-1</sup>. Additionally, the Si—O—Si crosslinks are concentrated in the gel (1040 cm<sup>-1</sup>), as would be expected. On the other hand, the soluble fraction does not show a band at 1660 cm<sup>-1</sup>. This result proves that unsaturation sites (as revealed by the appearance of the bands at 1660 cm<sup>-1</sup>) are concentrated in the gel, rather than in the soluble fraction, and are related to the Si—O—Si structure.

The first stage of silane crosslink formation is hydrolysis to form an intermediate silanol. We have tried to follow the hydrolysis using the disappearance of the bands at 800 and 1090 cm<sup>-1</sup> and the appearance of the band at 3549 (3431) cm<sup>-1</sup>, but these bands are very weak in intensity, so it is difficult to make quantitative measurements. Smith<sup>18</sup> mentioned that the methoxy group also

**Table I** Infrared Absorption Frequencies Used to Follow the Grafting and Crosslinking Reactions

Structure	Frequency (cm <sup>-1</sup> )	Reference
NH <sub>2</sub> stretch	3280	
NH	3320	
—Si—OCH <sub>3</sub>	800 (1090)	17, 18
—Si—OH		
Free	3691	18
Hydrogen bonded	3549 (3431)	19
—Si—O—Si—	1020–1100	17, 18
CH <sub>2</sub> —N stretching	1473	

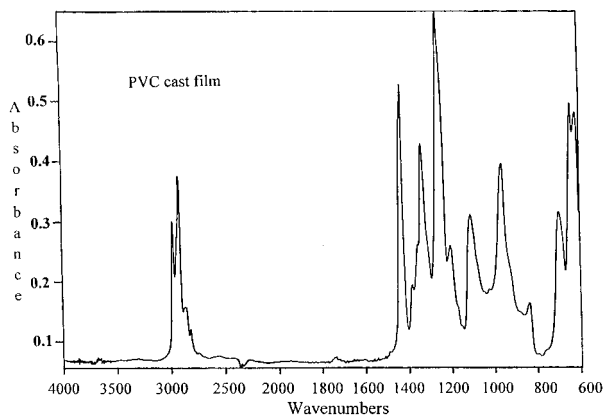


Figure 1 Infrared spectrum of virgin PVC.

has a characteristic absorption band at  $1250\text{ cm}^{-1}$ ; but in PVC, this band overlaps the C—H bending mode. Bullen et al.<sup>15</sup> and Hjertberg et al.<sup>16</sup> were able to follow these reactions in polyethylene and ethylene vinyl silanes copolymers, respectively. In their studies, they used commercial silane-grafted copolymers. In our study, we prepared the grafted material during processing; so it is likely that hydrolysis of methoxy groups occurred during processing, and, therefore, it was not possible to find methoxy groups in the grafted PVC.

To obtain a quantitative estimate of the structure formed during the grafting and crosslinking process, a baseline was traced on the IR spectrum, and the absorption intensities of some bands of interest were measured. The substitution reaction displaced chlorine atoms; consequently, a decrease in the absorption bands due to the C—Cl should be observed. Also, the bands due to Si—O—Si and Si—O—CH<sub>3</sub> should increase. Absorption ra-

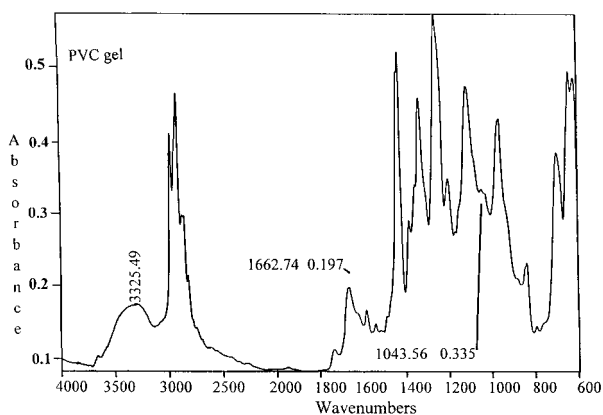


Figure 2 Infrared spectrum of crosslinked PVC.

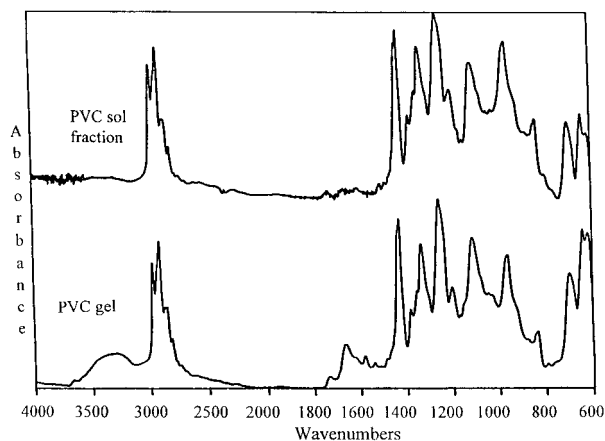


Figure 3 Infrared spectrum of (a) PVC soluble fraction and (b) PVC gel.

tios for the peaks arising from the structures listed in Table II were calculated using the absorption of C—C at  $1105\text{ cm}^{-1}$  as an internal standard. The same table also lists the characteristic configuration and conformational isomers associated with the C—Cl group frequencies according to Krimm et al.,<sup>23,24</sup> Pohl and Hummel,<sup>25</sup> and Robinson et al.<sup>26</sup>

Absorption ratios for the C—Cl structure and bands in the region of Si—O—CH<sub>3</sub> before crosslinking are shown in Figure 4. It can be seen that as the crosslinking agent concentration increases, the C—Cl absorption tends to decrease as a result of the reaction with the aminosilane. On the other hand, the Si—OCH<sub>3</sub> absorption increases. The bands in the region between  $1100$  and  $1000\text{ cm}^{-1}$  may either be due to Si—O—CH<sub>3</sub> or Si—O—Si because it is difficult to distinguish between the absorption frequencies of these two groups, as indicated by Smith.<sup>17,18</sup>

Similar trends were observed for the crosslinked polymer, as shown in Figure 5. The grafted polymer is very nearly crosslinked, as indicated by the quasi-quantitative transformation from the grafted to crosslinked structures, although it was not possible to demonstrate by direct measurements of the amount of Si—O—CH<sub>3</sub> and Si—O—Si, which are associated to the grafted and crosslinked polymers, respectively. However, IR analysis of the soluble fraction after Soxhlet extraction with THF did not show the characteristic bands of siloxanes. This suggests that almost all the grafted polymer is participating in the crosslinking reaction.

The absorption ratios of the other C—Cl structures were also analyzed. Figures 6 and 7 show

**Table II** Infrared Absorption Frequencies Used to Estimate the Degree of Substitution in Grafted and Crosslinked PVC

Structure	Frequency (cm <sup>-1</sup> )	Configuration	Conformation	Type of C—Cl
C—Cl	615	s	tttt	S <sub>HH</sub>
C—Cl	637	s	tttt	S' <sub>HH</sub>
C—Cl	692	i	tgtgtg	S <sub>HC</sub>
Si—O—Si	1030	—	—	—
Si—O—CH <sub>3</sub>	1024	—	—	—
C—CH <sub>2</sub>	1427	—	—	—

s = Syndiotactic; i = isotactic; t = trans; g = gauche.

the results for the grafted and crosslinked polymer, respectively; and it is interesting to observe in both figures that the C—Cl band at 637 cm<sup>-1</sup> tends to decrease (this was also observed with the band at 615 cm<sup>-1</sup>), while the band at 692 cm<sup>-1</sup> remains almost constant.

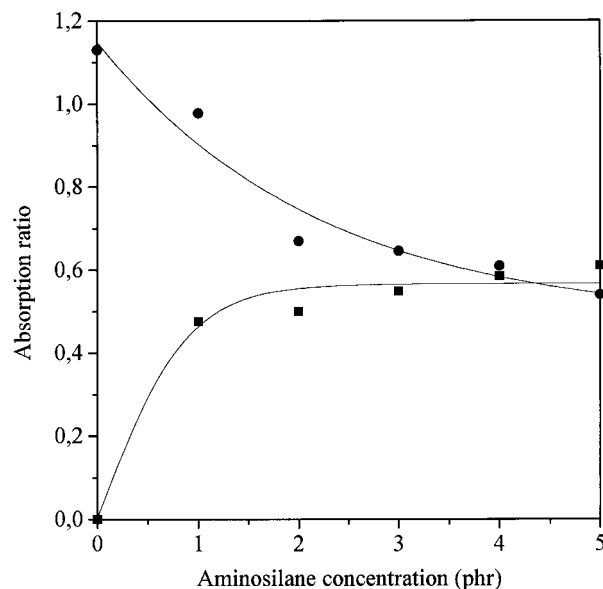
The bands at 615 and 637 cm<sup>-1</sup> are associated with a syndiotactic configuration and tttt conformation. According to these results, it is suggested that the syndiotactic sequences preferentially react during the grafting reaction, and the isotactic sequences associated with the absorption at 692 cm<sup>-1</sup> remain almost unmodified. It is reasonable to propose this mechanism since the steric hindrance is lower in the syndiotactic configuration. However, it is necessary to recall that the carbon—chlorine stretching region in the vibrational

spectrum does not offer a practical route for quantitative estimation of tacticity. In order to have a quantitative measurement of tacticity and to know exactly which structures are taking place during the grafting reaction, a nuclear magnetic resonance (NMR) study would be necessary.

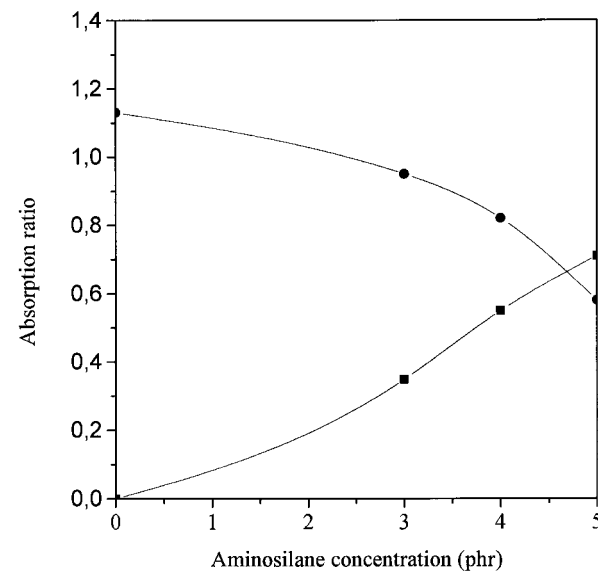
As discussed earlier, an absorbance band appears at 1660 cm<sup>-1</sup>, apparently associated with double bonds introduced during the grafting process. If an elimination reaction is taking place, some CH<sub>2</sub> groups would disappear. Figure 8 shows the absorption ratio for the CH<sub>2</sub> bending at 1427 cm<sup>-1</sup>. It can be seen that this band tends to decrease as the aminosilane concentration increases.

#### Gel Permeation Chromatography

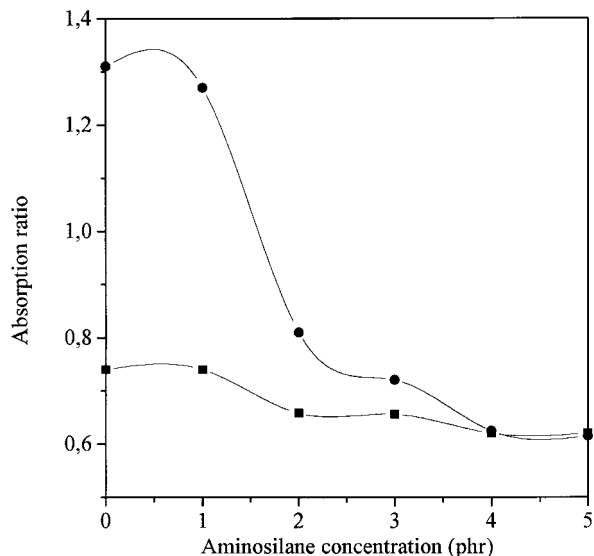
To detect molecular enlargement during processing, changes in the molecular weight and mo-



**Figure 4** Absorption ratios for the C—Cl and Si—OCH<sub>3</sub> bands of the grafted polymer: (●) C—Cl at 615 cm<sup>-1</sup>, (■) Si—O—CH<sub>3</sub> at 1045 cm<sup>-1</sup>.

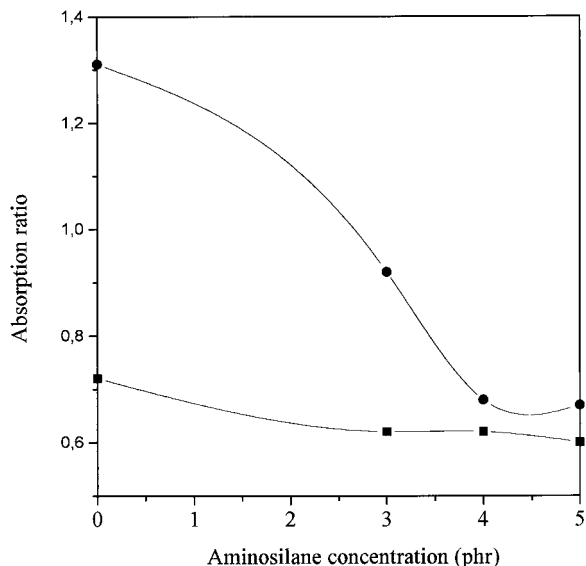


**Figure 5** Absorption ratios for the C—Cl and Si—OCH<sub>3</sub> bands of the gel fraction: (●) C—Cl at 615 cm<sup>-1</sup>; (■) Si—O—Si at 1045 cm<sup>-1</sup>.

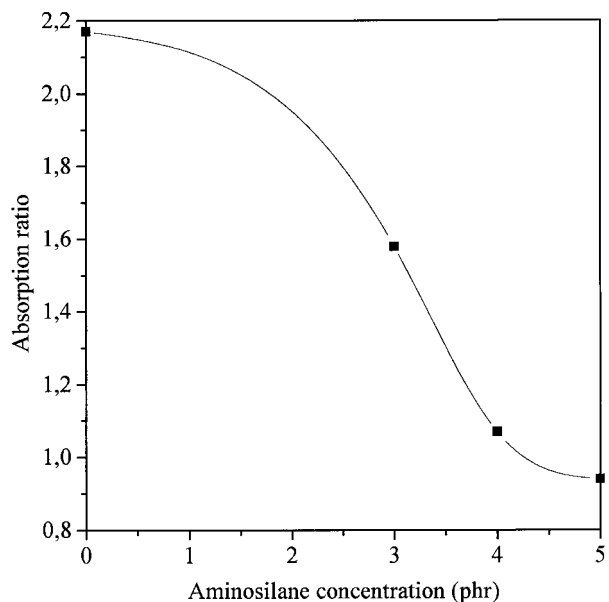


**Figure 6** Absorption ratios for the C—Cl bands of the grafted polymer: (■) C—Cl at  $692\text{ cm}^{-1}$ ; (●) C—Cl at  $637\text{ cm}^{-1}$ .

lecular weight distribution were followed by GPC. The samples were stabilised with 3 phr of tin stabilizer and were roll-milled at  $145^\circ\text{C}$  for different periods of time. The GPC analysis showed that extensive molecular enlargement occurred. This is demonstrated in Table III for samples containing 3 phr of aminosilane. Increases in both  $M_n$ , the number-average molar mass, and  $M_w$ , the weight-average molar mass, are observed.



**Figure 7** Absorption ratios for the C—Cl bands of the crosslinked polymer: (■) C—Cl at  $692\text{ cm}^{-1}$ ; (●) C—Cl at  $637\text{ cm}^{-1}$ .



**Figure 8** Absorption ratios for the  $\text{CH}_2$  band of the grafted polymer: (■)  $\text{CH}_2$  at  $1427\text{ cm}^{-1}$ .

The  $M_w$  results are plotted in Figure 9 for various aminosilane concentrations. It can be seen that as the aminosilane concentration increases,  $M_w$  increases. This is what would be expected as larger molecules have a higher probability of participating in crosslinking reactions.<sup>27</sup> Similar trends were observed for  $M_n$ . It is interesting to note also that  $M_n$  increases as much as 120% without formation of gel. When 1 phr of aminosilane was used, both  $M_w$  and  $M_n$  increased continuously. With 2 phr, a maximum in both  $M_w$  and  $M_n$  was observed after 5 minutes; and when 3 phr were used, the maximum was reached at 2 minutes before both values decreased. This maximum, followed by a decrease in molecular weight, could be associated with either chain scission due to degradation or formation of gel. The first mecha-

**Table III** Changes in Molecular Weight Due to Milling at  $145^\circ\text{C}$  for a Sample Containing 3 phr of Aminosilane

Milling Time (min)	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	$M_w/M_n$
1	3.29	1.5	2.18
2	3.47	1.83	1.89
3	3.31	1.74	2.03
5	2.89	1.49	1.94
8	2.59	1.35	1.92

$M_w$  of virgin PVC = 121,000;  $M_n$  of virgin PVC = 71,000.

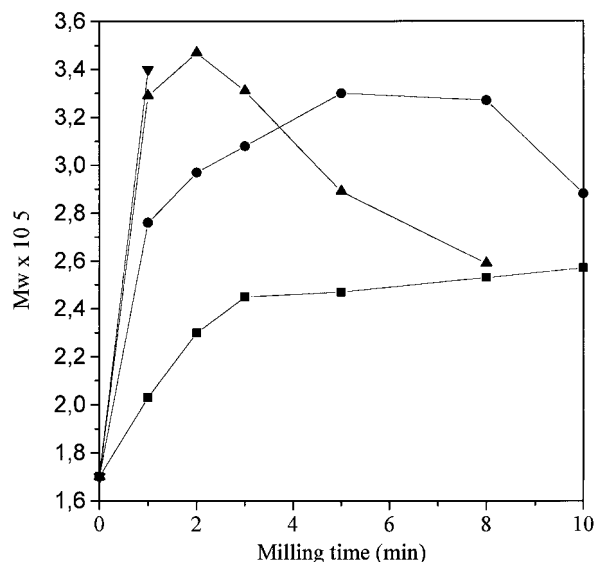
nism is unlikely to occur because PVC does not normally degrade by chain scission. To verify the second mechanism, the milled sample containing 3 phr of aminosilane was Soxhlet extracted, and the maximum was shown to be associated with the formation of gel.

The large increase in  $M_n$  suggests that, besides the normal random reaction with normal PVC units, a more specific reaction favoring low-molecular-weight polymer could be taking place. The observed increase in molecular weight and the decrease in  $M_w/M_n$  indicates that some terminal groups preferentially react with the crosslinking agent. On the other hand, the soluble fraction from the crosslinked polymer had a very low molecular weight. Hjertberg et al.<sup>11</sup> used <sup>1</sup>H-NMR to show that for PVC crosslinked with dithioltriazines, 1-chloro-2-alkene structures have a high reactivity towards substitution.

### Crosslinking Density

After Soxhlet extraction, the crosslinking density was evaluated for the insoluble fractions. Table IV shows the results of crosslinking density and  $M_c$  of samples crosslinked with different levels of aminosilane.

As a result of increasing crosslinking agent concentration, an increase in crosslinking density is observed, as expected. However, at first sight,  $M_c$  seems to be high as the  $M_n$  of the pure PVC is



**Figure 9** Dependence of  $M_w$  on milling time for samples containing different levels of aminosilane: (■) 1, (●) 2, (▲) 3, and (▼) 4 phr.

**Table IV** Molecular Weight Between Crosslinks

Z 6020 Concentration (phr)	Crosslinking Density $\times 10^5$ (mol cc)	$M_c$ (g mol)
1	3.31	42 040
2	4.38	31 770
3	5.99	23 200
4	6.80	20 450

70,000 g mol. Also, the  $M_c$  of these samples seem high compared with the results obtained by Nethsinghe and Gilbert<sup>27</sup> for PVC crosslinked by radiation. However, due to the molecular enlargement detected in the grafted polymer before crosslinking, they look more reasonable. The reaction mechanism with aminosilane is more specific than that taking place in radiation crosslinking.

### CONCLUSIONS

Infrared analysis proved to be useful for following the changes between the original PVC and the gel. —Si—O—Si— was detected in the region between 1020 and 1090  $\text{cm}^{-1}$ . In this region, it has been reported that the structures —Si—OCH<sub>3</sub> and Si—OH, associated with the grafted and hydrolyzed grafted PVC, are also both IR active, so it was not possible to differentiate between the three structures.

Frequencies associated with the CH—Cl vibrational mode can be detected, and the method is sensitive enough to detect the reduction in concentration of these structures as a result of the substitution reaction.

The syndiotactic structures seem to be more reactive than the isotactic towards grafting and subsequent crosslinking. Double bonds produced as a result of secondary reactions were also detected by IR analysis. These structures were concentrated in the gel and are associated with the crosslinked structure.

A significant increase in molecular size was observed, associated with long processing times in combination with a highly reactive formulation containing a high content of aminosilane. This underlines the necessity of carefully adjusting the formulation in order to avoid problems during processing.

It is suggested that some terminal structures are taking part in the grafting process, causing

an increase in molecular weight. This is supported by the fact that compared to the molecular weight of the normal PVC, the molecular weight between crosslinks is high for samples crosslinked with both low and high concentrations of crosslinking agent.

An increase in crosslink density of the gel was observed as a result of increasing the crosslinking agent concentration.

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