Reaction Rate and MWD Changes in Crosslinking of PVC, with Dithioltriazine

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Synopsis

The reaction rate of crosslinking of PVC with dithioltriazine has been studied by following gel formation and changes in the molecular weight distribution (MWD). Compounding was performed on a roll mill at 145°C and crosslinking by heat treatment at 180 or 90°C. In this system crosslinking is executed by the thiolate anion, formed *in situ* by reaction with MgO. We have studied the catalyzing effect of several polyols in order to achieve a more efficient reaction. Most likely, these catalysts work by chelating the Mg^{2+} ions, thus increasing the nucleophilic character of the thiolate. With the most efficient ones, ditrimethylolpropane and $HO(CH_2CH_2)_{6-7}H$, complete crosslinking can be obtained in 3 min at 180°C, i.e., at processing temperatures. We also followed the changes in the MWD before gelation at a considerably lower temperature, 145°C, and found an extensive molecular enlargement even after 5–10 min. Most surprisingly, $\overline{M}_n$ increased up to 100% without formation of insoluble material. By ^1H-NMR measurements on low molecular weight extracts, we have shown this to be due to a fast and selective reaction with allylic chlorine in the unsaturated end groups, $\sim CH_2{-}CH{=}CH{-}CH_2Cl$, formed in the mechanism of chain transfer to monomer. Due to this reaction, formulations with too high reactivity may crosslink during processing, which calls for a careful balancing of the reactivity for each processing case.

INTRODUCTION

The extensive use of PVC is partly due to the large possibilities to vary the mechanical properties by the addition of plasticizer. Although plasticized PVC is used at temperatures well above T_g, the properties are favorable and the material has a rubberlike behavior. This is generally considered to be due to the presence of a physical network consisting of small crystallites.[1] At temperatures above 50°C, however, plasticized PVC will flow under mechanical load.

One way to increase the maximum application temperature of plasticized PVC is to introduce a permanent chemical network. For the production of cables, a commercial process exists which is based on radical crosslinking initiated by radiation. In order to minimize the necessary radiation dose and accompanying dehydrochlorination, rather large amounts of "reactive plasticizers" (e.g., trimethylolpropanetriacrylate) are added.[2-4] It is, however, also possible to utilize the fact that the carbon—chlorine bond is polarized and can be broken by a nucleophilic attack. By using a polyfunctional nucleophile with appropriate properties, crosslinks can thus be introduced. The basicity of the reagent should not be too large, as in, e.g., amino groups, as this generally leads to elimination of HCl.[5] Being a strong nucleophile and a weak base, the

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thiol group is an attractive alternative. In a series of papers Mori and Nakamura have discussed the use of dithioltriazines for the crosslinking of PVC.[6-10] By converting, e.g., 2-dibutylamino-4,6-dithiol-*s*-triazine (DB) to a metal salt, they have been able to obtain complete crosslinking in reasonable times without simultaneous dehydrochlorination.

Crosslinking of a thermoplastic is normally a two-step procedure. First, compounding and forming are performed under conditions which should not activate the crosslinking reactions. The latter is instead performed in a second step, often at somewhat increased temperature. The low thermal stability of PVC, however, heavily limits the maximum applicable thermal load. The rate of a thermally activated crosslinking reaction, e.g., a nucleophilic substitution, should thus be as high as possible. The reactivity should, on the other hand, not be high enough to cause molecular enlargement or even crosslinking prematurely. In this paper we first discuss the effect of certain catalysts on the rate of crosslinking of PVC with DB. The major part deals, however, with the changes in the molecular weight distribution (MWD) during compounding. The relation between these changes and the presence of structures including chlorine with enhanced reactivity compared to the ordinary secondary chlorine has also been investigated.

EXPERIMENTAL

Materials

The PVC used in this investigation was a suspension PVC from KemaNord AB (now NorskHydro Plast AB), Sweden (S 706; $\bar{M}_n = 50{,}000$; $\bar{M}_w = 127{,}000$). 2-dibutyl-4,6-dithioltriazine (Ziznet DB, Sankyo Kasei Corp.) was used without further purification as were magnesium oxide (extra pure, Merck), ditrimethylolpropane (DITMP, Perstorp AB), polyol 217 (Perstorp AB), polyoxyethylene-laurylether (Brij 35, Kebo Grave AB), stearic acid (Naftozin N, Metall Gesellschaft AG) and di-2-ethylhexyl-phtalat (Beroxo AB). For thermal stabilization Naftovin T3 (tribasic lead sulfate, Metall Gesellschaft AG) and Swedstab BTMS 40 (tin maleate and mercaptide mixture, Swedstab AB) were used.

Processing and Crosslinking

After dry mixing, liquid components (plasticizer and BTMS 40) were added under agitation. The mixture was then rolled on a two-roll laboratory mill for 5, 10, or 15 min at 145°C to sheets with a thickness of 1 mm. To achieve crosslinking, samples were treated at 180°C in a hydraulic press. In some cases crosslinking was performed at 90°C in a forced-air oven.

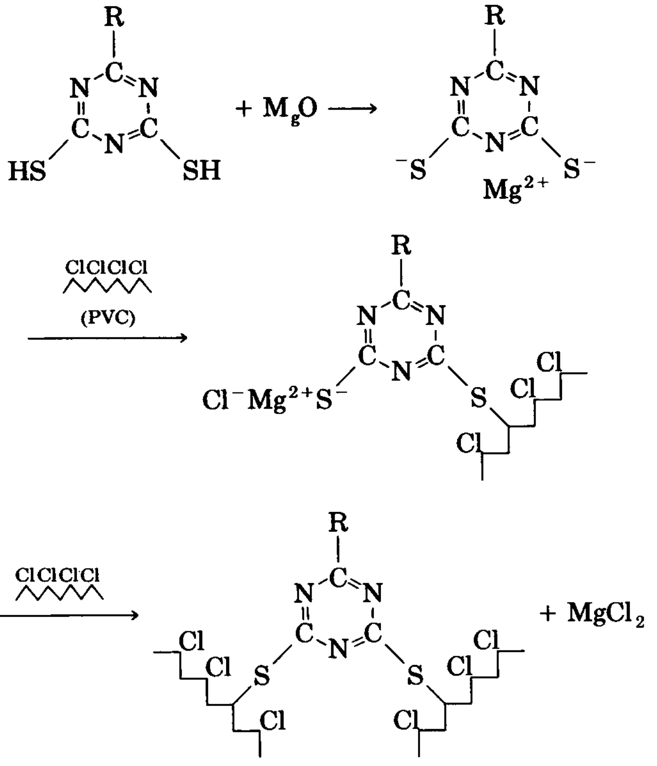
Analysis

The gel content was determined by Soxhlet extraction overnight with peroxide-free tetrahydrofuran. The amount of extracted polymer was determined gravimetrically after concentration of the eluate (250 to ca. 25 mL), precipitation in 300 mL methanol, filtration, and drying in vacuum.

Gel chromatography (GPC) and viscometry were used for determination of MWD and degree of long chain branching (LCB). Intrinsic viscosity was determined in tetrahydrofuran at 25°C with an Ubbelohde viscometer. No correction for kinetic energy losses was necessary. A Waters Associates GPC Model 200 operating at 25°C with tetrahydrofuran as solvent was used. The column combination consisted of five Styragel columns with permabilities ranging from 10^3 to 10^7 Å, giving good separation in the molecular weight range of interest. To calculate molecular weight averages and LCB, the computer program devised by Drott and Mendelson[11] was used The calibration for linear PVC was obtained via the universal calibration curve. Experimental details have been given earlier.[12]

RESULTS AND DISCUSSION

If DB is used as such, crosslinked PVC is obtained but with simultaneous dehydrochlorination.[7] There are evidences that crosslinking at least partly occurs via the nitrogen atoms in the isocyanuric ring. If an acid acceptor such as MgO is added, the crosslinking rate increases and virtually no dehydrochlorination occurs.[7] Mori and Nakamura[7] have given the following reaction scheme for the reaction between PVC and DB in the presence of MgO:



(1)

(2)

(3)

It may be pointed out that the structure of the magnesium dithioltriazine salt (Mg–DB) is only represented schematically. The magnesium ion can not bind to both thiolate ions in one molecule as its radius is not large enough. A structure including the dimer or oligomers is much more plausible.

The increased rate in the presence of MgO is an effect of converting the thiol group to a thiolate anion, which is a stronger nucleophile. The reaction rate should increase with increased polarization of the thiolate—metal bond, i.e., with decreased electronegativity of the metal. This was indeed found by Mori and Nakamura who reported increased crosslinking rate in the series Sn < Pb < Mg < Ca < Ba.[8]

It should also be noted that reaction ⟨1⟩ is considerably faster than ⟨2⟩.[7] This is a consequence of the fact that the first thiol group is much more easily dissociated than the second one, the pK_a values vary between 4–6 and 11–14, respectively. The exact value, and thus the reaction rate, is determined by the third substituent on the triazine ring.[8]

Although conversion to a thiolate salt increases the crosslinking rate, the time to reach complete crosslinking may still be too long. Mori and Nakamura have therefore pointed out the necessity of adding certain accelerating compounds, such as polyethers.[7] In their published work[6–10] they have mostly used a polyethylene–oxide–laurylether (Brij 35), but in patents[13] several other suitable compounds are mentioned as well, e.g., polyfunctional alcohols.

Figure 1 shows how the content of gel increased with time of heat treatment at 180°C for a formulation containing 3 phr DB and 3 phr MgO. The solid line represents an experiment without added catalyst and the dashed line one with 1 phr Brij 35. These results are very similar to those reported earlier for corresponding formulations.[7] Without any catalyst, 100% gel was not obtained within the experimental time, 25 min. The use of 1 phr Brij 35 decreased the time for 100% gel formation to 15 min. Such an improvement is, however, hardly enough for practical use of this process.

In order to increase the reaction rate furthermore, we have tested several polyfunctional alcohols, or polyols, normally used as costabilizers in PVC. Such compounds often show synergistic effects in combination with thermal

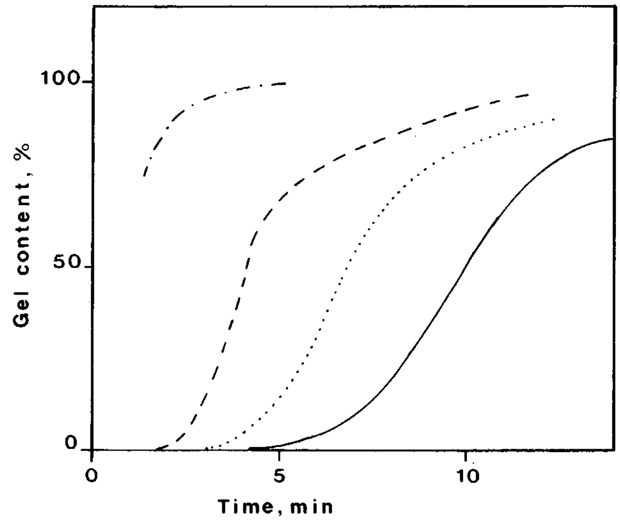


Fig. 1. Gel content (based on PVC) as a function of time of heat-treatment at 180°C. Formulation: PVC 100 phr; DOP 40 phr; DB 3 phr; MgO 3 phr; lead stabilizer 2.5 phr; (—) no catalyst; (- - -) Brij 35 1 phr; (- · -) DITMP 1 phr; (· · ·) polyol 217 1 phr.

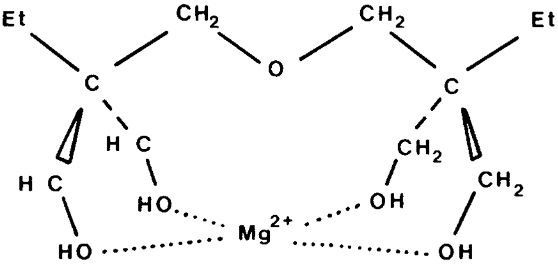


Fig. 2. Complex formation between DITMP and Mg^{2+}.

stabilizers based on metal soaps.[14,15] The best results were obtained with a dimer of trimethylolpropane (DITMP). As shown by the dash dotted line in Figure 1, the addition of 1 phr DITMP gives a much faster crosslinking than the same formulation, but with 1 phr Brij 35, 100% gel is reached after 3 and 15 min, respectively. Due to heating-up effects, shorter times than 2 min were not investigated. The results with another polyol, polyol 217, are shown as well in Figure 1. Compared to DITMP its efficiency as catalyst is, however, quite moderate.

The catalytic effect of DITMP can reasonably be explained by the possibility of the four hydroxyl groups coordinating with metal ions, e.g., Mg^{2+} (see Fig. 2). This coordination can be compared with crown ethers which are effective as complexing agents and are used as phase transfer catalysts.[16] A coordination between DITMP and Mg–DB could explain the effect on the crosslinking in two ways. First, the shielding of the polar part of Mg–DB by DITMP should lead to increased solubility and mobility. Second, the coordination should increase the polarization between Mg^{2+} and the thiolate ions. This should increase the nucleophilic strength and thus the reaction rate. Eventually, total dissociation might occur giving free thiolate ions. This would be comparable to the "naked anions" discussed in connection with crown ethers.

Although DITMP and polyol 217 are quite similar in structure, the former is much more effective as catalyst. A space-filling molecular model of DITMP shows that the four hydroxyl oxygens and the ether oxygen can form a cage with an approximate diameter of 2.5 Å, which effectively should coordinate metal ions. According to the producer, polyol 217 consists of two units of pentaerythritol connected by a spacer group. The distance between the two active units is thus longer, which makes the formation of a cage corresponding to that of DITMP more difficult. Alternatively, coordination might take place with the three remaining hydroxyls at one end of the molecule. In both cases the coordination capability should, however, be lowered compared to that of DITMP. This is in agreement with the difference observed in crosslinking rate.

The use of poly(ethylene glycol) as phase-transfer agent has been discussed in other contexts, see, e.g., Ref. 17. The polyethylene–oxide part of Brij 35 should be able to coordinate metal ions in a similar way as crown ethers. On the other hand, the polyether chain is longer than that necessary to form the structure corresponding to 18-crown-6 (Fig. 3). This and the presence of the

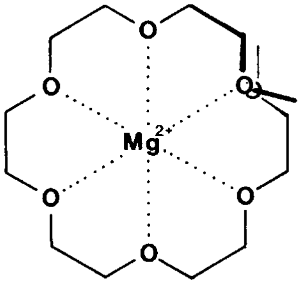


Fig. 3. Complex formation between Mg^{2+} and part of a polyethyleneoxide chain.

alkyl group should contribute to the rather low efficiency of Brij 35 on a weight basis.

Figure 3 implies that $HO(CH_2CH_2O)_{6-7}H$ (PEG 300) would be a suitable candidate as catalyst. Accordingly, Mori[18] has shown that a maximum in crosslinking rate was obtained for PEG with a molecular weight of 300 when PEGs of different molecular weights were tested. A comparison between PEG 300 and DITMP showed that these have about the same efficiency when added in the same molar amount (Fig. 4). Observe that the crosslinking was performed at 90°C in this case and that the amount of DITMP was as low as 0.3 phr. These conditions were chosen to enable a differentiation between these efficient catalysts which both give 100% gel within 3 min at 180°C.

The crosslinking rate demonstrated by the dash dotted line in Figure 1 is much higher than reported earlier[7] for the system DB–MgO. This has several advantages if the system should be used in industrial production of crosslinked PVC. The reduced thermal load necessary to obtain crosslinking will, of course, lead to a higher level of residual stability. The high reactivity is also positive from an economical point of view as it allows a faster production and/or reduces the demands for heating zones after forming. The crosslinking rate must, however, not be so high that the processing is impaired.

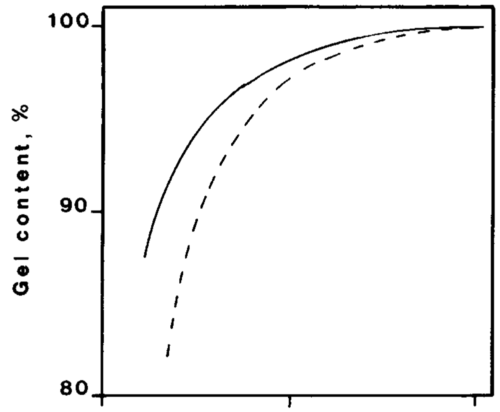


Fig. 4. Gel content (based on PVC) as a function of time of heat-treatment at 90°C. Formulation as given in Figure 1 but for the catalyst; (—) DITMP 0.3 phr; (- - -) PEG 300 0.36 phr.

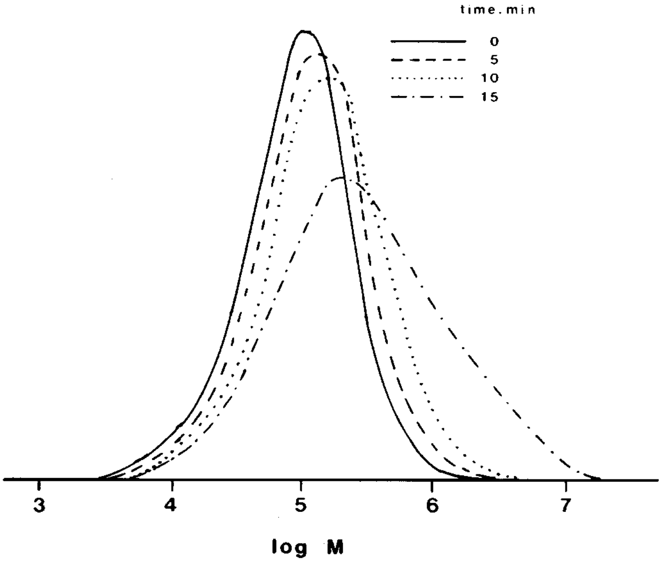


Fig. 5. The effect of roll milling at 145°C on the MWD. The formulation is given in Table I, sample 3.

To detect molecular enlarging reactions during processing, changes in the MWD were followed by GPC. The same basic formulation as above was used without any catalyst, and with 1 phr Brij 35, and 0.5 phr DITMP, respectively. After mixing, the samples were processed by roll milling at 145°C for 5, 10, and 15 min. Soxhlet extraction did not give any evidences of gel formation in any of these samples.

The GPC analysis showed, however, that extensive molecular enlargement had occurred. This is demonstrated in Figure 5 with the behavior of the sample with 1 phr Brij 35. Already after 5 min the MWD had shifted clearly toward higher molecular weights, and after 15 min the MWD had broadened considerably. According to our experience, gel formation should have occurred after only a few minutes additional processing time. In the case of the DITMP samples, it was impossible to filtrate the GPC solutions (0.5 μm filter), despite the fact that the Soxhlet extraction did not indicate any gel. Obviously, the molecular enlargement must have been excessive in these samples.

The molecular weight averages of all measurable samples are given in Table I. For comparison, the values of a sample processed for 5 min containing no MgO and DB are included as well. The latter are very close to those of the virgin polymer, indicating that the mild processing conditions did not influence the MWD by crosslinking due to degradation to any appreciable extent.

The large changes in the MWD for the samples with 1 phr Brij 35 are reflected by the drastic increase in $\overline{M}_w$, i.e., from 1.2×10^5 in the virgin polymer up to 5.3×10^5 after 15 min. Even in the samples without added catalyst, molecular enlarging reactions must have occurred as $\overline{M}_w$ was increased up to 1.9×10^5. This seems to be in disagreement with the results reported by Mori and Nakamura.[7] For a similar formulation they indicated an induction period of about 17 min at 160°C. The changes in the MWD were, however, not directly followed. Rheological measurements were used instead

TABLE I
Changes in Molecular Weight Data due to Compounding in a Roll Mill at 145°C

Sample	Time of compounding (min)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$[\eta]$ (dL/g)
1[a]	5	51	139	2.7	0.99
2[b]	5	56	148	2.6	1.13
	10	63	179	2.8	1.20
	15	64	194	3.0	1.43
3[c]	5	69	167	2.4	1.14
	10	84	229	2.7	1.40
	15	102	529	5.1	1.28

[a] PVC 100 phr; DOP 40 phr; lead stabilizer 2.5 phr; stearic acid 0.5 phr.
[b] As 1 + DB 3 phr; MgO 3 phr.
[c] As 2 + Brij 35 1 phr.

as an indirect measure. It may be presumed that the given induction period refers to the time for gel formation.

It is obvious that the use of an effective crosslinking catalyst such as DITMP might introduce molecular enlargement even at rather mild conditions. This should be noticed, in particular for processes where high shearing rates are employed, as friction may result in high temperatures, at least locally. The increased molecular weight would cause a further temperature rise due to the increased melt viscosity. This may eventually lead to complete crosslinking within the processing equipment. it is therefore very important to optimize the reactivity in each case with regard to the process used.

Table I shows that $\overline{M}_w$ increased relatively more than $\overline{M}_n$. This is what could be expected as larger molecules have a higher probability of participating in crosslinking reactions.[19] It is more noteworthy that $\overline{M}_n$ increased as much as 100% without gel formation. In the case of crosslinking during thermal degradation we have earlier observed an increase of only ca. 20% in $\overline{M}_n$ before gel was detected[20] for a sample with similar molecular weight. The large increase of $\overline{M}_n$ in the present investigation implies that, besides the random reaction with normal PVC units, a more specific reaction favoring low molecular weight material should be operative as well.

In addition to the normal structural units, PVC contains a number of irregular structures (see, e.g., Ref. 21). Some of these structures include chlorine in allylic position or on tertiary carbon, i.e., thermally labile structures. According to our opinion, tertiary chlorine in connection with ethyl, butyl, and long chain branches is the most important labile structure followed by internal allylic chlorine.[21-24] The increased thermal lability of such structures should also be followed by increased chemical reactivity. In earlier investigations attempts were consequently made to determine the total content of labile chlorine by substitution reactions, e.g., with phenol.[25-27] It has, however, been shown that this reagent also reacts with the unsaturated end group, 1-chloro-2-alkene,[28] formed in the mechanism for chain transfer to monomer Although the allylic chlorine thus is chemically activated, it has been shown to be thermally stable.[29]

TABLE 2
Yield and Molecular Weight Averages of Extracted Fractions

Sample[a]	Yield (%)	$\overline{M}_n$	$\overline{M}_w$
1	0.39	5600	9000
2	0.16	5600	9300
3	0.43	6200	9200
4	0.23	6200	9900

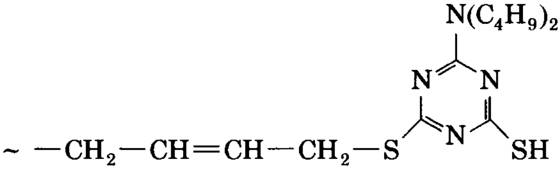
[a] PVC 100 phr; DOP 40 phr: (1) lead stabilizer 2.5 phr; (2) as 1 + DB 3 phr; MgO 3 phr; DITMP 0.5 phr; (3) tin stabilizer 1 phr; (4) as 3 + DB 3 phr; MgO 3 phr; DITMP 0.5 phr.

In principle, the above-mentioned structures should also show increased reactivity towards DB. However, the contents of both tertiary and internal chlorine are only weakly dependent on the molecular weight,[22,23] and these structures should therefore not be responsible for the unexpected large increase in $\overline{M}_n$. The content of 1-chloro-2-alkene is, of course, directly related to the molecular weight (0.7–1 per molecule[28,29]), and this structure is a plausible candidate to explain the behavior of $\overline{M}_n$ during processing. This implies a high reactivity towards DB, which is supported by the fact that the allylic chlorine in allylchloride is completely substituted by DB at 80°C.[7] However, one of the functions of most thermal stabilizers is to react with labile or more reactive chlorine. It has, e.g., been shown that dioctyl-tin-bis-2-ethylhexylthioglycolate reacts with the 1-chloro-2-alkene end groups at 180°C, i.e., at processing temperatures.[30] In a formulation containing both DB and a thermal stabilizer capable to react with activated chlorine, there might therefore be a certain competition.

To investigate if the 1-chloro-2-alkene structure reacts with DB and/or the thermal stabilizer, the behavior with two different stabilizers was studied. One of them was tribasic lead sulfate, which should be unreactive towards labile chlorines. The other was a commercial tin stabilizer, containing both tin maleate and tin mercaptide, which reasonably should substitute activated chlorine. Both stabilizers were used in formulations with and without DB (see Table II), and the samples were roll milled for 5 min at 145°C. In order to more easily detect eventual changes in the end groups by NMR, low molecular weight fractions were obtained by extraction (acetone–hexane, 3:1). As seen in Table II, all extracts had similar molecular weight, indicating the selectivity of the solvent used. The lower amount of extract obtained from the formulations containing DB is another indication of a selective reaction favoring low molecular weight material.

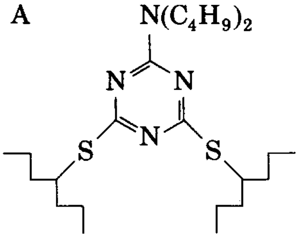
The H-NMR spectrum of the lead stabilized formulation without DB is given in Figure 6. Besides the major peaks representing $—CH_2—$ and $—CHCl—$ in the repetitive units, some smaller peaks originating from end groups (and chloromethyl branches) can be seen between 3.5–4.2 and 5.6–6.0 ppm (for complete assignments, see Refs. 28 and 30). These ranges of chemical shifts are also given at larger magnification with the peaks belonging to the 1-chloro-2-alkene end groups marked. The content of this structure was determined to ca. 12 per 1000 monomer units, or 1.1 per molecule. A similar value was also obtained for a corresponding extract of the original polymer. It is somewhat higher than obtained for whole polymers, 0.7–0.8 per molecule.[28] The same content of 1-chloro-2-alkene end groups was also determined in the sample without DB but stabilized by tin compounds; i.e., none of the two stabilizers reacts with the unsaturated end groups under the conditions employed in the present investigation (5 min at 145°C). This is much milder than those used by van den Heuwel and Weber,[30] who observed 25% substitution after 110 min at 180°C.

Figure 7 shows the H-NMR spectrum obtained with the low molecular weight extract of the sample containing DB and lead stabilizer. As seen in the magnification, the doublet at 4.05 ppm assigned to the CH_2Cl protons in the 1-chloro-2-alkene groups has disappeared. At the same time, the olefinic protons have shifted ca. 0.1 ppm upfield, and a new peak has appeared at about 3.45 ppm. A similar spectrum was observed for the extract obtained from the sample containing tin stabilizer and DB. Obviously, the chlorine has been substituted, and the observed changes are in accordance with the structure expected after reaction with DB:

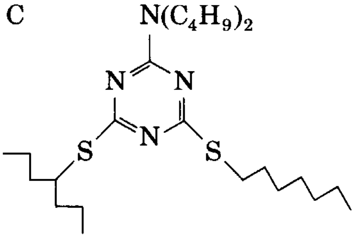


If the second thiol group subsequently substitute another chlorine, an allylic or ordinary secondary chlorine, it is easy to explain the participation of low molecular weight fractions at an early stage of the reaction. In contrast to the normally expected branch points with four arms (A), this selective reaction will lead to linear molecules (B) or branch points with three arms (C), respectively:

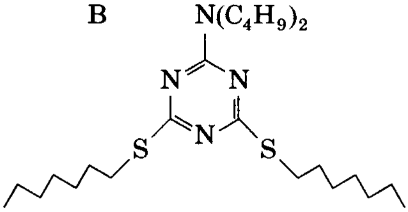
A



C



B



In a completely random crosslinking process, the probability for inclusion in the network decreases with decreasing molecular weight. The selective molecular enlargement discussed above is therefore advantageous as the subsequent crosslinking operation is facilitated. Such a molecular enlargement may,

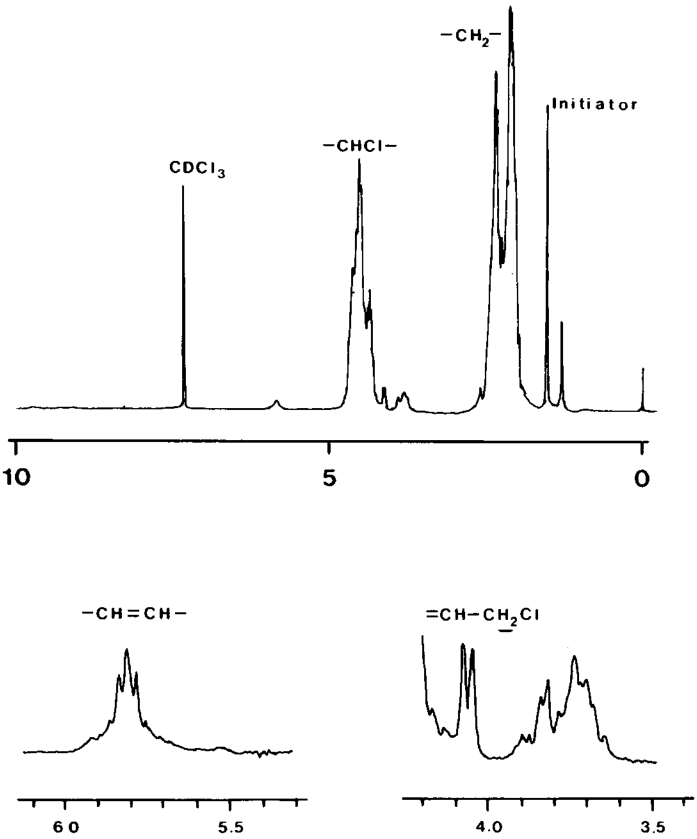


Fig. 6. 200 MHz ^{1}H-NMR spectrum of low molecular weight extract of sample 1 in Table II; 2% in $CDCl_3$; chemical shifts given in ppm vs. TMS.

however, be disadvantageous during processing as the melt viscosity should tend to increase. Long processing time in combination with a reactive formulation is therefore unsuitable as gel may form more easily than indicated by high temperature experiments. Obviously, this effect is at direct variance with the desire to obtain a fast crosslinking after the processing. This underlines the necessity of carefully adjusting the reactivity for each processing case.

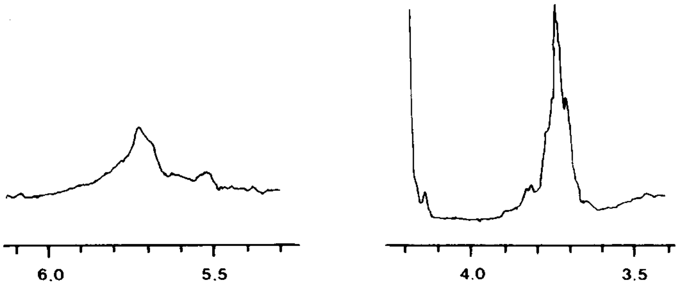


Fig. 7. 200 MHz ^{1}H-NMR spectrum of low molecular weight extract of sample 2 in Table II; conditions as in Figure 6.

CONCLUSIONS

The rate of crosslinking in the reaction between PVC and DB in the presence of MgO can be considerably increased by the addition of DITMP. This is suggested by an effect of coordination between DITMP and the Mg–DB salt formed. The four hydroxyl groups in DITMP may coordinate to the Mg ion by forming a selective cage, similar to the mode of action of crown ethers.

Although no gel is formed during processing with the conditions used, GPC analysis showed that extensive molecular enlargement occurs. The changes in the MWD indicated that a selective reaction favoring low molecular weight material should be operative. ^{1}H-NMR measurements on low molecular weight extracts showed that DB effectively reacts with the allylic chlorine in the 1-chloro-2-alkene end groups which explains the MWD-changes.

The presented results show that the time to complete crosslinking can be decreased to at least 2–3 min. However, due to the fast and selective reaction between DB and 1-chloro-2-alkene end groups, formulations with too high reactivity may crosslink during processing. A safe, effective, and economical production of crosslinked PVC using dithioltriazine, therefore, needs careful balancing of the reactivity.

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