

# New Aminated PVC Compounds: Synthesis and Characterization

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Received 29 October 1998; accepted 23 March 1999

**ABSTRACT:** Different compounds for the synthesis of poly(vinyl chloride) (PVC) with tertiary amino groups were tested, and the course of the modification reactions was followed under different conditions by nuclear magnetic resonance spectroscopy and elemental analysis. It is shown that PVC can be modified without side reactions with 2-mercaptopyridine, 2-mercaptopyrimidine, 4-mercapto-*N,N*-dimethylaniline, and 4-mercaptopyridine. The reactivity of the para-substituted mercapto compounds is found to be considerably higher than that of the corresponding ortho products, and higher final degrees of modification are achieved. The availability of the amino group towards electrophilic attack in order to form quaternary ammonium salts was tested by reaction with methyl iodide. While this reaction takes place in good yields in the case of PVC modified with 4-mercaptopyridine and 4-mercapto-*N,N*-dimethylaniline, aminated PVC with the nitrogen atoms in ortho position do not react due to steric hindrance by the polymer chain. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1178–1185, 1999

**Key words:** poly(vinyl chloride) (PVC); modification; aminated PVC; ionomers

## INTRODUCTION

The preparation of aminated polymers is of great industrial interest due to potential applications as polymeric proton-selective electrode materials or membranes for gas separation. In this respect, poly(vinyl chloride) (PVC) is an especially attractive polymer because of its excellent film-forming and membrane properties.

Modification of PVC can generally be achieved by nucleophilic substitution reactions of chlorine atoms. Appropriate modification agents are characterized by a strong nucleophile character, while

their basicity should be low in order to avoid dehydrochlorination.<sup>1,2</sup>

If modification of the polymer is carried out in order to introduce functional groups,<sup>3</sup> which can also react by a substitution mechanism, a second type of side reaction may occur, which is the crosslinking of the polymeric chains. To avoid crosslinking, the modification reaction has to be performed with a selective bifunctional molecule, of which only one functionality reacts with the polymer, while the other does not.

The functionalization of PVC with amino groups is an objective pursued by scientists for more than 10 years.<sup>4–7</sup> The general approach to achieve this aim was the use of aliphatic diamines. This, however, caused problems due to the elevated basicity of these compounds. Furthermore, the absence of selectivity of the modification agents forced the substitution reaction to be stopped at relatively low conversion to limit crosslinking.

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Contract grant sponsor: Comision Interministerial de Ciencia y Tecnología (CICYT); contract grant number: MAT 96-0615.

*Journal of Applied Polymer Science*, Vol. 74, 1178–1185 (1999)

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CCC 0021-8995/99/051178-08

**Table I** Reaction Conditions for the Modification of PVC with 4-MP, 2-MP, 2-MPm, and 4-MDMA

Entry Number	Modification Agents (Molar Ratio)	<i>T</i>	Solvent	Reaction Time (h)	DOM (%)	Observations
1	PVC-2-mercapto pyridine-K <sub>2</sub> CO <sub>3</sub> (1 : 1 : 1.5)	60°C	CH	20	27.0	yellow
2	PVC-2-mercapto pyridine sodium salt (1 : 1)	60°C	CH	42	17.4	nearly white
3	PVC-2-mercapto pyridine sodium salt (1 : 1)	45°C	DMF	3	17.1	orange
4	PVC-2-mercapto pyrimidine-K <sub>2</sub> CO <sub>3</sub> (1 : 1 : 1.5)	60°C	CH	19	13.7	nearly white
5	PVC-2-mercapto pyrimidine sodium salt (1 : 1)	60°C	CH	9	5.1	white
6	PVC-4-mercapto- <i>N,N</i> -dimethylaniline-K <sub>2</sub> CO <sub>3</sub> (1 : 1 : 1.5)	60°C	CH	16	35.3	white
7	PVC-4-mercapto- <i>N,N</i> -dimethylaniline sodium salt (1 : 1)	60°C	CH	1	40.1	white
8	PVC-4-mercapto- <i>N,N</i> -dimethylaniline-K <sub>2</sub> CO <sub>3</sub> (3 : 1 : 2)	60°C	CH	19	14.2	white
9	PVC-4-mercapto pyridine-K <sub>2</sub> CO <sub>3</sub> (1 : 1 : 1.5)	60°C	CH	20	—	brown
10	PVC-4-mercapto pyridine-K <sub>2</sub> CO <sub>3</sub> (1 : 1 : 1.5)	45°C	DMF	4.5	8.9	slightly yellow
11	PVC-4-mercapto pyridine sodium salt (1 : 1)	60°C	CH	8	41	white
12	PVC-4-mercapto pyridine sodium salt (1 : 1)	40°C	DMF	3	3.4	white

DOM is the degree of modification.  
CH is cyclohexanone, and DMF is dimethyl formamide.

In previous work,<sup>8,9</sup> we described the modification of PVC with primary and tertiary aromatic amino groups, respectively, using 4-mercaptoaniline (4-MA) and 4-mercaptopyridine (4-MP). The substitution reactions are extremely selective with respect to the mercapto group, and the copolymers formed are neither crosslinked nor polluted by any other kind of side products. Furthermore, it was shown that this type of reaction is stereoselective and can be performed in solution, melt, or suspension.<sup>10-13</sup>

It has also been shown<sup>9</sup> that PVC with pendant pyridine groups can easily be transformed to yield ionomers<sup>14-19</sup> and polyelectrolytes when reacted with alkyl iodides. These products have potential applications as ion exchange resins. However, as 4-mercaptopyridine is not very economic, alternative compounds have to be found.

In the present article, we describe the synthesis of aminated PVC with new commercial as well as noncommercial mercapto compounds and investigate their transformation to ionomers.

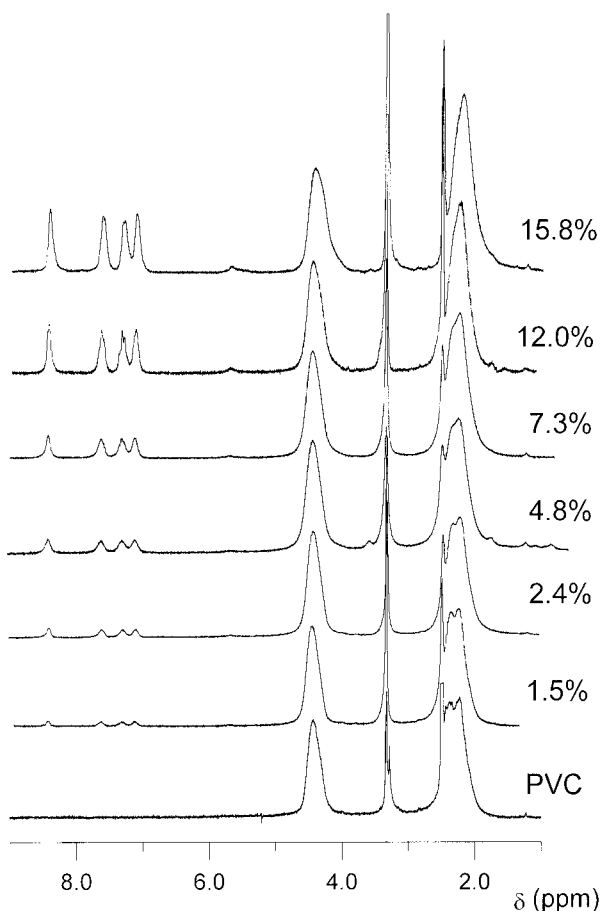
## EXPERIMENTAL SECTION

### Materials

Commercial, bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by gel permeation chromatography (GPC) were  $M_w = 112,000$  g/mol and  $M_n = 48,000$  g/mol. The tacticity measured by <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) was syndio = 30.6%, hetero = 49.8%, and iso = 19.6%.

Cyclohexanone was bidistilled prior to use, diethyl ether was dried by refluxing and distillation over lithium aluminium hydride. Tetrahydrofuran (THF) was distilled after drying over sodium. All other compounds used in synthesis were commercial high-purity grade and used without further purification.

2-Mercaptopyridine (2-MP) and 2-mercaptopyrimidine (2-MPm) were purchased from Aldrich. The <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra of both compounds can be found in Pouch-



**Figure 1** Evolution of the  $^1\text{H-NMR}$  spectra in  $\text{DMSO-d}_6$  upon conversion for the modification of PVC with 2-MP sodium salt.

ert and Behnke<sup>20</sup> and Aksnes.<sup>21</sup> The corresponding sodium salts were obtained by reaction with stoichiometric amounts of sodium hydride [60% dispersion in mineral oil (Aldrich)] in THF and pyridine, respectively. After 24 h at room temperature, the solutions were filtered, and the white salts were precipitated and washed with hexane.

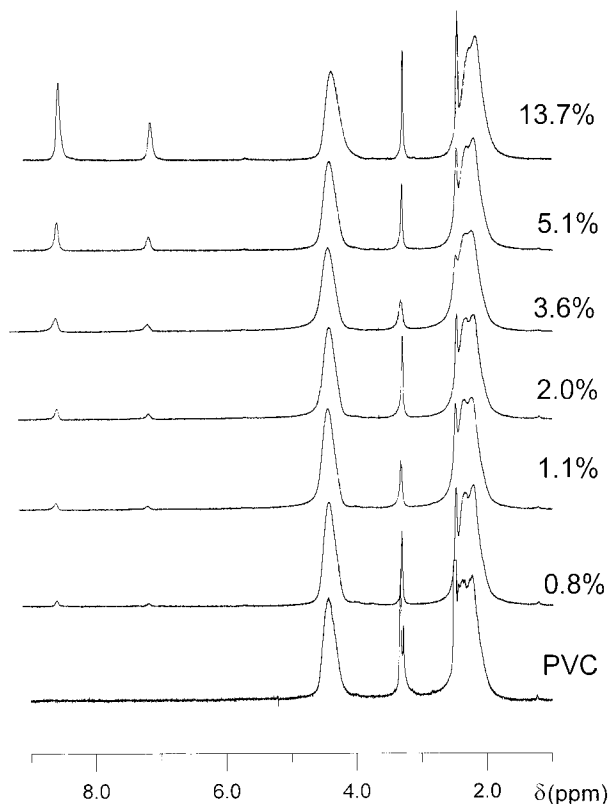
4-Chlorosulfonyl-*N,N*-dimethylaniline (**1**) was synthesized by chlorosulfonation of *N,N*-dimethylaniline with chlorosulfonic acid. A five-fold molar excess of acid was used, and the reaction mixture stirred for 18 h under a nitrogen atmosphere at 120°C. The mixture was then diluted with dichloromethane and poured into ice. The organic phase was separated and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was stripped off, and the residue was crystallized from nitrogen-saturated heptane obtaining yellow crystals.  $^1\text{H-NMR}$  in  $\text{CDCl}_3$ :  $\delta = 7.85$  (d, 2 ArH), 6.7 (d, 2 ArH), 3.05 (s, 6 H). Yield: 15%.

4-mercapto-*N,N*-dimethylaniline (4-MDMA) was synthesized by reduction of **1** with a triple

molar amount of lithium aluminium hydride ( $\text{LiAlH}_4$ ) in THF. The reaction mixture was refluxed for 6 h. The solvent was then substituted by diethylether, and the excess of  $\text{LiAlH}_4$  was destroyed with ice. 15%  $\text{H}_2\text{SO}_4$  was carefully added, the phases separated, and the organic phase washed with water and dried over  $\text{Na}_2\text{SO}_4$ . Then the ether was stripped off, and the residue was distilled under reduced pressure ( $\text{bp}^{0.5 \text{ Torr}}$ : 97°C).  $^1\text{H-NMR}$  in  $\text{CDCl}_3$ :  $\delta = 7.5$  (d, 2 ArH), 6.7 (d, 2 ArH), 3.35 (s, SH), 2.95 (s, 6 H). Yield: 80%.

#### Modification of PVC with Mercapto Compounds

8 mmol of PVC [based on monomer units ( $M = 62.5 \text{ g/mol}$ )] and 8 mmol of the respective mercapto compound were dissolved in 50 mL of the solvent, 1.6 g potassium carbonate was added (only in the cases where the mercapto compound is used instead its sodium salts), and the reaction was started under a  $\text{N}_2$  atmosphere at 60°C (for cyclohexanone) or 45°C (for dimethyl formamide), respectively. The reaction was stopped by precipitating the mixture in cold methanol/water (2 : 1).



**Figure 2** Evolution of the  $^1\text{H-NMR}$  spectra in  $\text{DMSO-d}_6$  upon conversion for the modification of PVC with 2-MPm sodium salt.

**Table II Comparison of Degrees of Modification of Aminated PVC Compounds Obtained by Elemental Analysis and H-NMR**

Sample	NMR $X (\%) \pm 0.5$	Elemental Analysis (%)			
		C (%)	H (%)	N (%)	$X (\%) \pm 0.3$
PVC	0	38.4	4.80	0	0
PVC-2MP	17.4	40.6	4.54	1.91	16.8
PVC-2MPm	5.1	39.0	4.51	1.21	5.6
PVC-4MP	65.7	47.9	4.62	6.73	63.2
PVC-4MDMA	40.1	49.7	5.63	3.31	41.2

$X$  is the molar percentage of aminated PVC monomer units.

The modified polymers were purified using THF/methanol or THF/hexane as a solvent-precipitant system.

#### Quaternization of the Modified PVCs

0.5 g (7 mmol) aminated PVC was dissolved in 30 mL of nitrobenzene, a five-fold molar excess (with respect to the aromatic groups in the polymer) of methyl iodide was added, and the solution was stirred for 2 days at 35°C. The solution was then precipitated in hexane, and the product was purified in a Soxhlet extractor with hexane during 24 h. Yield was 95%.

#### Characterization

Degrees of substitution of PVC, expressed as mol % of ethyl thio aryl ether units/(ethyl thio aryl

ether units + ethyl chloride units), were determined by  $^1\text{H-NMR}$ . Spectra were recorded in 5–10% ( $w/v$ ) solutions with a Varian Gemini 200, (200 MHz,  $T = 25^\circ\text{C}$ ; 16 scans; pulse width, 20  $\mu\text{s}$ ). The solvents were purchased from Scharlau (DMSO- $d_6$ ,  $\text{CDCl}_3$ ) and Aldrich (nitrobenzene- $d_5$ ) and had levels of deuteration of 99.8% (DMSO,  $\text{CDCl}_3$ ) and 99.5% (nitrobenzene), respectively.

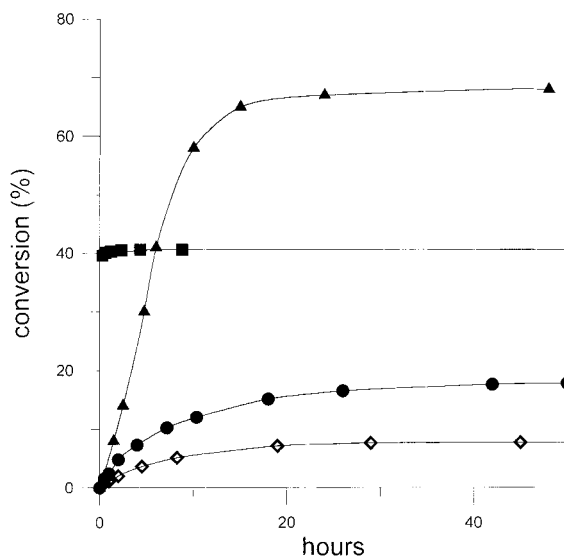
## RESULTS AND DISCUSSION

For the modification of PVC with tertiary amino groups, 2-mercaptopyridine (2-MP) and 2-mercaptopyrimidine (2-MPm) have been tested as alternatives to 4-mercaptopyridine (4-MP). These compounds exhibit a similar chemical structure as 4-MP but have the advantage to be considerably less expensive.

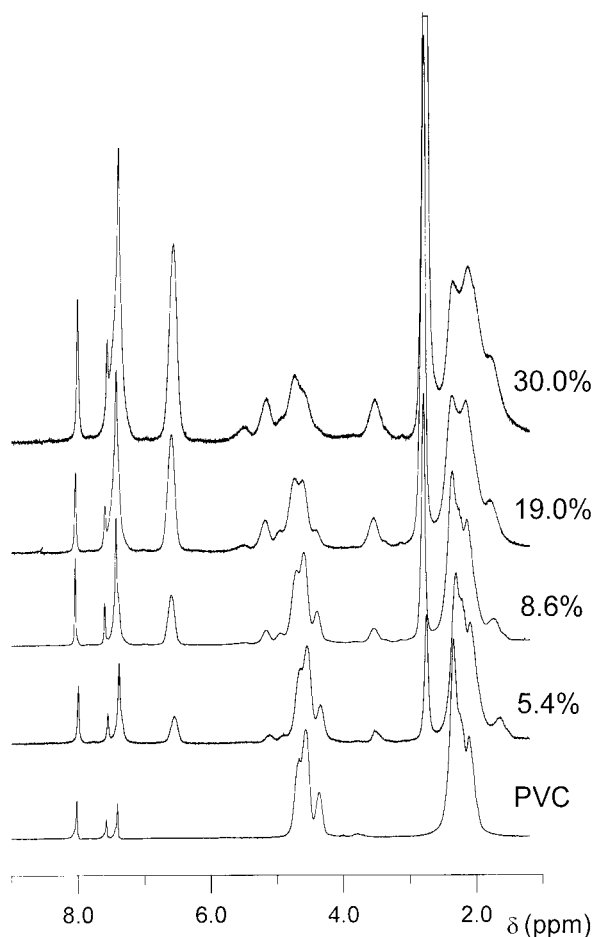
#### Modification with 2-Mercaptopyridine and 2-Mercaptopyrimidine

In previous work,<sup>3,8,9</sup> the optimal conditions for the nucleophilic substitution reactions with mercapto compounds on PVC have been found to be with cyclohexanone (CH) or dimethylformamide (DMF) as the solvents at 60°C (in the case of CH) and at 45°C (in the case of DMF) as the reaction temperature. As the nucleophile, the thiol compound, together with potassium carbonate as the base or the sodium salt of the compound, can be used. When using the thiol compounds in equimolar quantity with respect to PVC, the reaction has reached maximum conversion after 15–20 h; while using their sodium salts, the equilibrium state is reached after 3–6 h.

The results of the modification of PVC with 2-MP and 2-MPm under these reaction conditions are compared in Table I (entry numbers 1–3 and



**Figure 3** Conversion of the modification reactions of PVC with 4-MP ( $\blacktriangle$ ), 2-MP ( $\bullet$ ), 2-MPm ( $\diamond$ ), and 4-MDMA ( $\blacksquare$ ) as a function of time.



**Figure 4** Evolution of the  $^1\text{H}$ -NMR spectra upon conversion for the modification of PVC with 4-MDMA sodium salt.

4–5, respectively). Interestingly, in both cases, using the thiol compound together with potassium carbonate yield considerably higher degrees of modification than the use of the corresponding sodium salt of the thiol. This is in contrast to what has been found with other aromatic thiols.<sup>3</sup> With 4-mercaptopyridine (entry number 9), for example, modification with the pure compound in CH is not possible without strong degradation of the PVC, while the reaction with the sodium salt (entry number 11) gives a highly modified white polymer.

In Figures 1 and 2,  $^1\text{H}$ -NMR spectra in DMSO- $d_6$  and their evolution upon conversion of PVC modified with 2-MP and 2-MPm sodium salt are shown. In both cases, a growth of aromatic proton peaks is observed with increasing reaction time, while neither the signal at 4.5 ppm corresponding to the CH—Cl protons nor

the position or intensity of the  $\text{CH}_2$  protons at 2.2 ppm change with conversion. The existence of new formed CH—S protons, which appear in the present case obviously in the same region than the CH—Cl signal, has been proven for analogous compounds by detailed  $^{13}\text{C}$ -NMR studies.<sup>10</sup> Dehydrochlorination, which would lead to the formation of olefinic proton peaks at 5.8 ppm, is strongly suppressed under the given conditions and can be appreciated only to a very small extent (0.3%) for the highest modified samples. Other kinds of side reactions do not occur either, as is indicated by the good agreement of theoretical and experimental values of the elemental analysis (Table II).

The degree of modification  $X$  of PVC-2MP and PVC-2MPm can easily be determined from the NMR spectra according to eqs. (1) and (2), respectively, where  $I(\delta)$  corresponds to the integrals of the areas below the signal.

$$X (\text{PVC-2MP}) = I(7.0\text{--}8.6 \text{ ppm}) / [4 \cdot I(4.5 \text{ ppm})] \quad (1)$$

$$X (\text{PVC-2MPm}) = I(7.0\text{--}8.8 \text{ ppm}) / [3 \cdot I(4.5 \text{ ppm})] \quad (2)$$

In Figure 3, the conversion of the modification reactions of PVC with 2-MP and 2-MPm is shown as a function of time and compared with that of 4-MP. It can be seen that both thiols with nitrogen in the ortho position reach overall lower degrees of conversion when compared to 4-MP. This huge difference in the reactivity of nucleophiles of similar structure has its origin in electrostatic neighbor group effects, which are known to occur in reactions on polymeric materials when charged or partially charged particles are involved. The free electron pair of the nitrogen of a formed PVC-2MP or PVC-2MPm unit prevents the approach of a thiolate molecule to the chlorine atoms in its neighborhood by electrostatic repulsive forces. Reactivity differences between 2-MP and 2-MPm are due to the fact that the latter exhibits two electronegative centers near the sulfur atom, which lowers its electron density and thereby deactivates the nucleophile center of the molecule.

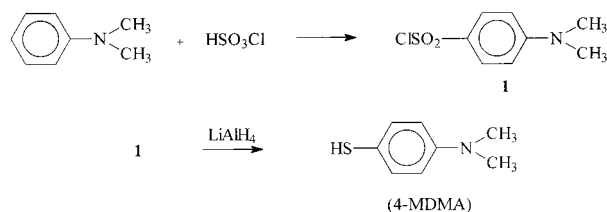
#### Modification with 4-Mercapto-*N,N*-Dimethylaniline

An other kind of modification agents capable to react with PVC forming an aminated polymer are

aromatic thioles, which exhibit an amino functionality outside the aromatic ring. In previous work,<sup>7</sup> we described the synthesis of PVC modified with mercapto-aniline to yield a material with pendent primary amino groups. The maximum degree of modification in this case was found to be about 30% due to strong polymer-polymer interactions caused by hydrogen bonding. The limited chain mobility related to such interactions may cause problems in certain applications of this material. The synthesis of an analogous polymer with tertiary amino groups where hydrogen bonding does not exist should therefore be an interesting alternative.

The appropriate compound for this purpose might be 4-mercapto-*N,N*-dimethylaniline (4-MDMA), which is not commercial and has been synthesized in our laboratory in a two-step reaction. In the first step, 4-chlorosulfonyl-*N,N*-dimethylaniline (**1**) is obtained by a classical aromatic chlorosulfonation starting from the inexpensive raw materials *N,N*-dimethylaniline and chlorosulfonic acid. The yield of this reaction is rather low due to the deactivation of the aromatic ring by formation of a quaternary ammonium salts when adding the acid. (**1**) is reduced in the second step using lithium aluminium hydride to give the desired mercapto compound 4-MDMA. The synthetic route is shown in Scheme 1.

Modification of PVC with 4-MDMA has been performed in CH at 60°C using either the compound together with potassium carbonate or the sodium salt directly (Table I). In Figure 4, the <sup>1</sup>H-NMR spectrum and its evolution upon conversion for the reaction is shown. The highly modified polymer is very easily soluble in chloroform but has become insoluble in dimethyl sulfoxide. Therefore, spectra have been recorded in deuterated nitrobenzene, which is a good solvent for all samples, independent of the degree of modification of the polymer. At 6.6 and 7.5 ppm, two new signals corresponding to the para-substituted aromatic ring protons appear. At 2.9 ppm, the peak of the two amino methyl groups arise, whose area



Scheme 1

integrates the triple of each of the aromatic proton peaks. The signal of the CH—Cl protons between 4.4 and 4.7 of pure PVC, which is split up (4.6, 4.5, 4.4 ppm) in nitrobenzene due to iso-, hetero-, and syndiotactic sequences of the chains has become more complex and has broadened, originated by the effect of the chemical composition distribution of the polymer upon modification, which means by methine protons of chlorine centred triads, which have one or two substituted groups in their neighborhood (new peak at about 5.0 ppm). The peak arising at 3.6 ppm can be attributed to the newly formed CH—S protons.

The degree of modification of the samples can be calculated from the spectra according to formula (3).

X (PVC-4MDMA)

$$= I(6.6 \text{ ppm})/2 \cdot I(6.0-3.2 \text{ ppm}) \quad (3)$$

Using the reaction conditions indicated in Table I, high degrees of modification of 35–40% are reached. Dehydrochlorination is not observed, and, consequently, white fine powders are obtained. Elemental analysis confirms the purity of the aminated polymer (Table II).

The course of the modification reaction of PVC with 4-MDMA is shown in Figure 3. In comparison with 2-MP, 4-MP, and 2-MPm, the newly synthesized mercapto compound is the most rapid one. After only 15 min of reaction time, the equilibrium state is reached. This elevated velocity is due to the fact that the nitrogen atom is situated outside the aromatic ring and increases the electron density of the system by a positive mesomeric effect, while the electron density is reduced in the case of the heteroaromatic mercapto compounds because of the high electronegativity of the nitrogen atom(s). On the other hand, although 4-MDMA is a better nucleophile, the highest degrees of modification are achieved using 4-MP. This can be explained by the presence of the bulky methyl groups in 4-MDMA, which hinder the access of the compound to chlorine atoms in the vicinity of reacted units.

### Formation of Ionomers and Polyelectrolytes

Tertiary amines of low molecular weight can be transformed to quaternary amino salts under mild conditions when reacted with alkyl halides. This reaction can be made use of to introduce ionic groups into the aminated PVC systems. It

**Table III** Degrees of Quaternization Measured by H-NMR and Elemental Analysis

Sample	NMR $X (\%) \pm 0.5$	Elemental Analysis (%)				U (%)
		C (%)	H (%)	N (%)	$X (\%) \pm 0.3$	
PVC-2MP (12.2%)	0	40.3	4.92	1.18	0	0
PVC-2MPm (4.7%)	0	37.9	4.78	0.98	0	0
PVC-4MP (6.8%)	6.8	38.2	4.83	0.32	6.9	100
PVC-4MDMA (30%)	11.4	44.7	5.42	1.87	10.8	38

$X$  is the molar percentage of quaternized amino groups with respect to PVC monomer units.

$U$  is the percentage of quaternized amino groups with respect to tertiary amino groups present in the polymer.

has been shown that PVC-4MP does react quantitatively with alkyl iodides at room temperature when the reaction is carried out in nitrobenzene as the solvent.<sup>9</sup>

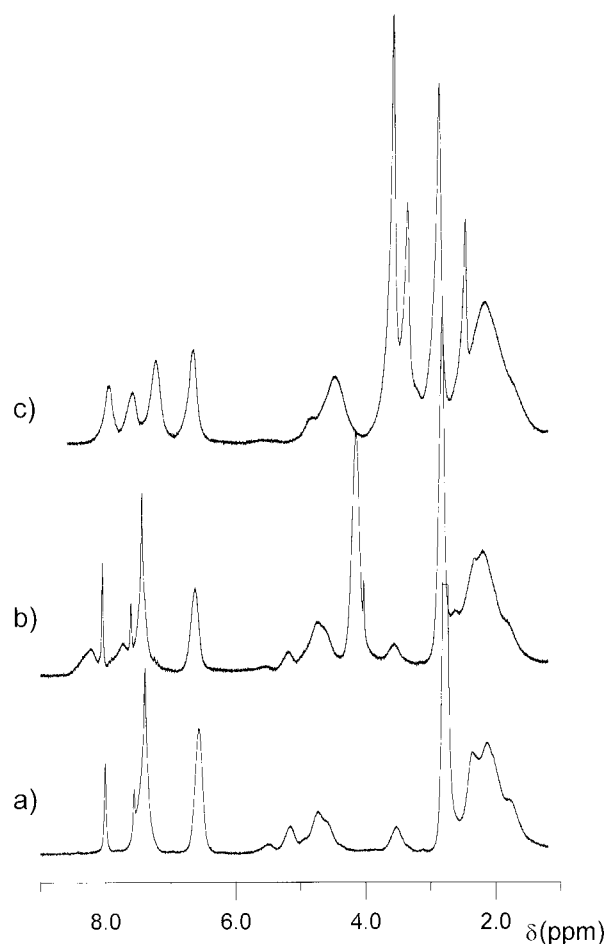
Analogous reactions have been carried out on PVC-2MP, PVC-2MPm, and PVC-4MDMA using methyl iodide as the most reactive alkylation agent. The conversion of the reaction can be followed by <sup>1</sup>H-NMR. The spectra of the polymers carrying ionic groups are characterized by two main features. On the one hand, a new methyl proton peak must appear in the aliphatic region. On the other hand, the quaternization of the heterocyclic as well as anilinic amino groups should lead to an impoverishment of the electron density of the ring system, yielding in a considerable shift of the aromatic proton peaks towards lower field. Additionally to the NMR analysis, elemental analysis was performed in order to confirm the structure of the obtained products.

The results of the quaternization reaction are summarized in Table III. While the aminated polymers PVC-2MP and PVC-2MPm do not at all react with methyl iodide under the given conditions in the PVC-4MDMA system, about 40% of the amino groups are transformed into ionic groups. The H-NMR spectra of PVC-4MDMA and the corresponding ionomer in deuterated nitrobenzene are shown in Figure 5(a) and (b). The new formed signal at 4.0 ppm can be attributed to the trimethylammonium groups. In the aromatic region, a new pair of signals appears at 7.6 and 8.1 ppm, which is partially covered by the peaks of the nitrobenzene. In order to allow an accurate calculation of the conversion  $X$ , the spectra of the ionomers were recorded in deuterated DMSO [Fig. 5(c)]. In this solvent,  $X$  is obtained using eq. (4).

$$X = 1 - [2 \cdot I(6.7 \text{ ppm}) / I(8.2 - 6.5 \text{ ppm})] \quad (4)$$

From the obtained results, it can be concluded that only the substituents carrying the nitrogen

atom in the para position to the polymeric chain are susceptible to the formation of quaternized ammonium salts, while the polymers with the reactive centers in the ortho position to the polymer do not react due to steric hindrance by the chains. The different reactivities of methyl iodide towards PVC-4MDMA and PVC-4MP (which re-



**Figure 5** <sup>1</sup>H-NMR spectra of PVC-4MDMA in deuterated nitrobenzene (a) and the corresponding ionomer in nitrobenzene (b) and DMSO (c).

acts quantitatively) are also caused by steric effects, as the  $sp^2$ -hybridized nitrogen of a pyridine ring is more easily accessible than the nitrogen in a  $sp^3$ -hybrid state with three bulky substituents like in an anilic structure.

## CONCLUSION

2-Mercaptopyridine, 2-mercaptopyrimidine, and 4-mercaptodimethylaniline are suitable compounds to introduce tertiary amino groups in PVC chains. The reactivity of the agents differs strongly and depends on the position of the nitrogen atom in the ring. In all cases, reaction conditions can be found, which allow chlorine substitution without the occurrence of side reactions.

It has been shown that 4-mercaptodimethylaniline can be used as inexpensive alternative to 4-mercaptopyridine for the synthesis of PVC carrying ionic groups. A comparative study of the mechanical properties and ion exchange capability of both ionomeric polymers is now in progress.

The authors thank the Comision Interministerial de Ciencia y Tecnología (CICYT) for financial support (No. MAT 96-0615).

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