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Synthesis and characterization of poly(vinyl chloride)-containing amino groups

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The synthesis of poly(vinyl chloride) (PVC) modified with *p*-aminothiophenol is described. The presence of free amino groups in the products is proven and their content measured by nuclear magnetic resonance and infrared spectroscopy, and elemental analysis. Modification degrees of up to 30% can be achieved without degradation or other side-reactions. The amino group containing polymers can be easily cross-linked or modified, yielding gels, networks or PVC with covalently bound plasticizers. © 1997 Elsevier Science Ltd.

(Keywords: PVC modification; aminated PVC; cross-linking; plastification)

Introduction

Poly(vinyl chloride) (PVC) is one of the most important commercial polymers due to its low production costs and its excellent stability to acids and bases. However, there are some shortcomings such as limited thermal and mechanical stability or sensitivity to ultraviolet radiation. By chemical modification reactions of PVC with appropriate compounds, new polymers with improved physical properties can be obtained[1–6]. A reaction that has been intensively studied in recent years is the nucleophilic substitution of chlorine atoms with thiophenolate. It was shown that this reaction is stereoselective and can be performed in solution, melt or suspension[7–11].

Recently we reported the possibility of PVC modifications with bifunctional agents such as *o*-thiobenzylalcohol, *p*-thiobenzylalcohol, mercaptosilanes and others[12,13]. If aromatic thiol compounds are employed, high degrees of substitution can be achieved, and no side-reactions, such as dehydrochlorination, are observed. We have found higher degrees of modification using *para*-substituted agents containing functional groups with positive inductive and mesomeric effects[12].

The functionalization of PVC with amino groups opens the way to a wide range of possibilities due to the high reactivity of amino groups *versus* condensation with acid chlorides. Thus, it should be possible to modify these amino group-containing polymers in a second step, introducing easily covalent bound plasticizers, dyes or u.v. stabilizers. Migration problems can be avoided in this way. Diacid chloride cross-linking of the modified PVC should be possible, improving the mechanical stability at higher temperatures. Amino group-containing polymers are also extensively studied as membranes with potentiometric response. Promising results have been found for PVC containing only 2.5% amino groups[14,15]. In the present paper we report the preliminary results of the modification of PVC with *p*-aminothiophenol, polymer characterization and polymer properties.

Experimental

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by gel permeation chromatography (g.p.c.) were $M_W = 112\,000\,\mathrm{g\,mol^{-1}}$ and $M_N = 48\,000\,\mathrm{g\,mol^{-1}}$. The tacticity measured by ^{13}C n.m.r. was syndio 30.6%, hetero 49.8% and iso 19.6%. *p*-Aminothiophenol was purchased from Acros. It was purified by distillation under reduced pressure (b.p. (4 torr) 112–115°C). ^{1}H n.m.r. ($(CD_3)_2SO$): $\delta = 7.05$ (d, 2 ArH), 6.5 (d, 2 ArH), 5.3 (s, NH_2), 4.6 (s, SH).

Dodecanoyl chloride and Adipoyl chloride were purchased from Fluka and used without further purification.

Cyclohexanone was bidistilled prior to use.

Modification of PVC. Four grams (64 mmol) of PVC, 8 g (64 mmol) of 4-aminothiophenol and 96 mmol of potassium carbonate were dissolved in 400 ml of cyclohexanone and allowed to react under an N_2 atmosphere at 60°C. At different time intervals, samples of 50 ml of the reaction mixture were withdrawn and precipitated in cold methanol/water (9:1) mixture. Purification was achieved using tetrahydrofuran (THF)/methanol (samples 1–4) and THF/hexane (samples 5–8), respectively, as the solvent–precipitant system.

Modification of PVC-NH_2. PVC-NH_2 (modification degree 6%; 1 g) was dissolved in 50 ml of dry THF. The solution was cooled down to 0°C, and a double molar quantity (with respect to the NH_2 groups) of dodecanoyl chloride in THF was added. After 30 min the reaction mixture was precipitated in methanol. Purification was achieved using THF/methanol as the solvent–precipitant system.

Characterization. Degrees of substitution of PVC, expressed as mole per cent of ethyl thioaniline/ethyl thioaniline + ethyl chloride, were determined by ^{1}H n.m.r., i.r. and elemental analysis. ^{1}H n.m.r. spectra were recorded at 25°C in 5% (w/v) dimethyl sulfoxide (DMSO)-*d* solutions with a Varian Gemini 200 MHz instrument under standard conditions. I.r. measurements

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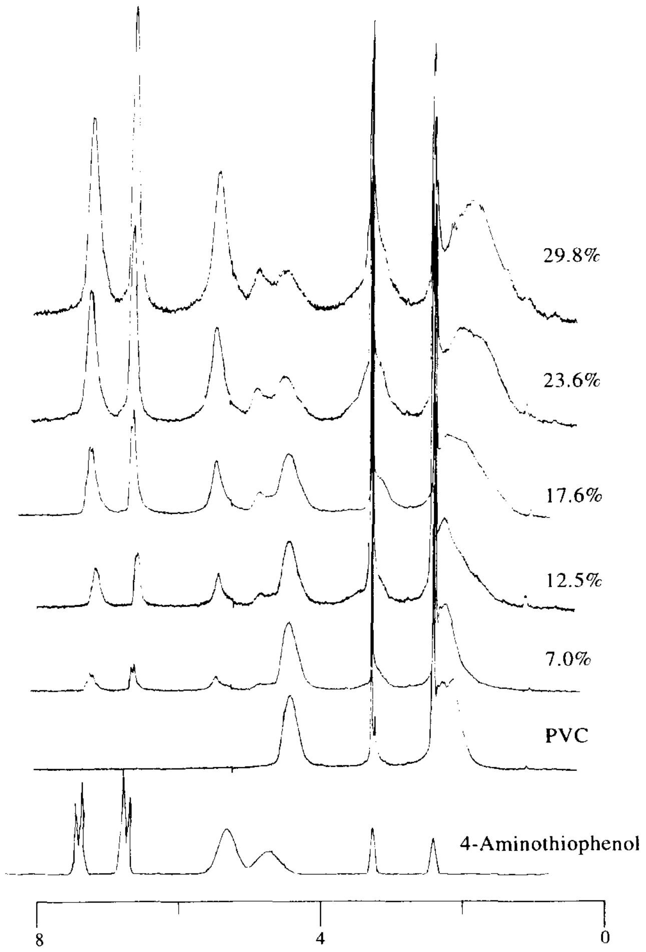

Figure 1 Evolution of the n.m.r. spectrum (in DMSO) of PVC during the modification reaction with 4-aminothiophenol

were performed on a Perkin-Elmer 783 i.r. spectrophotometer. Thermal properties were analysed on a Perkin-Elmer DSC7.

Results and discussion

Characterization of modified PVC. The modification reaction was performed as indicated in the Experimental section. At different time intervals, samples were withdrawn. After precipitation and purification they were analysed by ^{1}H n.m.r. spectroscopy.

In *Figure 1* the corresponding spectra of the PVC obtained at different modification degrees are shown. With increasing reaction time, aromatic (6.5 and 7.1 ppm) as well as amino proton peaks (5.2 ppm) arise. The signal at 4.5 ppm, corresponding to the CH–Cl protons, is lowered. Instead, two peaks at 4.8 and at 3.3 ppm are formed. The latter is partially covered by the H_2O peak, and is assigned to the CHS protons. Three important facts need to be pointed out:

- 4-Aminothiophenol is suitable to form PVC with free amino groups, as indicated by the n.m.r. peak at 5.2 ppm.
- The PVC chains react selectively with the thiol group of the modification agent. No chlorine atom is substituted by nitrogen. This can be deduced from the constant ratio (2:1) of the aromatic to the amino protons. Consequently, no cross-linking is observed; all obtained products were still THF-soluble.
- The modification reaction is free of any undesired side-reactions. No dehydrochlorination, causing peaks at 5.8 and 6.2 ppm, were observed. All products were white in colour.

The presence of free NH_2 groups in the polymer can also be shown by i.r. measurements, where three characteristic peaks between 3200 and 3500 cm^{-1} are formed due to N–H valence bonds (*Figure 2*). Additional peaks in the modified polymer can be assigned to the N–H deformation (1620 cm^{-1}), to the aromatic C–C valence bond (1600 and 1500 cm^{-1}), to the C–N valence bond (1180 cm^{-1}) and to the C–H deformation for *para*-substituted aromatics (820 cm^{-1}).

Kinetics of substitution. In order to be able to synthesize PVC with different and well-known contents of amino groups the kinetics of the substitution reaction was recorded. In previous work, the optimal reaction conditions for the nucleophilic substitution of the chlorine atoms in PVC by aromatic thiol compounds turned out to be cyclohexanone as the solvent, a reaction temperature of 60°C and potassium carbonate as the base[12]. These conditions were employed for the PVC modification with 4-aminothiophenol. The kinetics was followed by measuring the degree of modification of samples withdrawn at different reaction times by means of n.m.r., i.r. and elemental analysis.

From n.m.r. measurements the conversions U can be calculated according to equation (1), where $I(\delta)$ are the integrals of the areas below the resonance signal:

$$U = [I(6.5\,\text{ppm}) + I(7.15\,\text{ppm})]/4[I(4.5\,\text{ppm}) + I(4.8\,\text{ppm}) + I(5.2\,\text{ppm})/2] \tag{1}$$

In order to calculate conversions from the i.r. spectra a calibration curve was recorded. Therefore, the spectra of PVC/4-aminothiophenol mixtures of known composition were measured and the ratio of the integrals

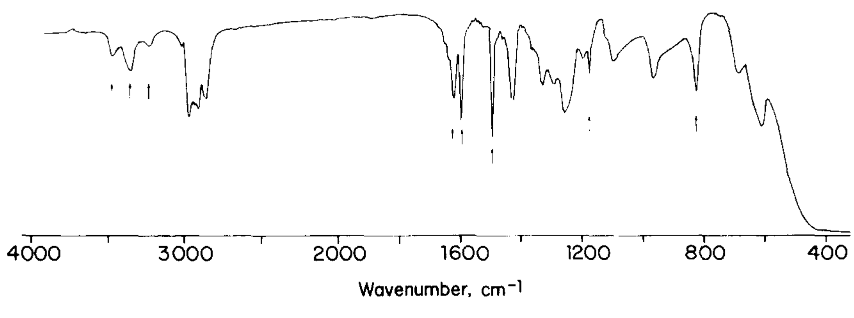

Figure 2 I.r. spectrum of PVC modified with 4-aminothiophenol (modification degree 8%)

Table 1 Comparison of the degree of modification, U, determined by n.m.r., i.r. and elemental analysis

Time (min)	N.m.r. $U(\%) \pm 0.5$	I.r. $U(\%) \pm 1$	Elemental analysis (%) C	H	N	$U \pm 0.1$
0	0	0	38.4	4.80	0	0
20	7.0	6	42.4	4.98	1.46	7.0
40	12.5	13	44.7	5.01	2.32	12.2
80	17.6	18	47.0	5.27	3.19	17.9
140	23.6	25	49.6	5.35	4.22	25.7
360	28.7	27	51.1	5.39	4.61	29.1
600	29.7	30	51.9	5.44	4.98	32.5
1440	29.8	30	52.0	5.46	5.06	33.2

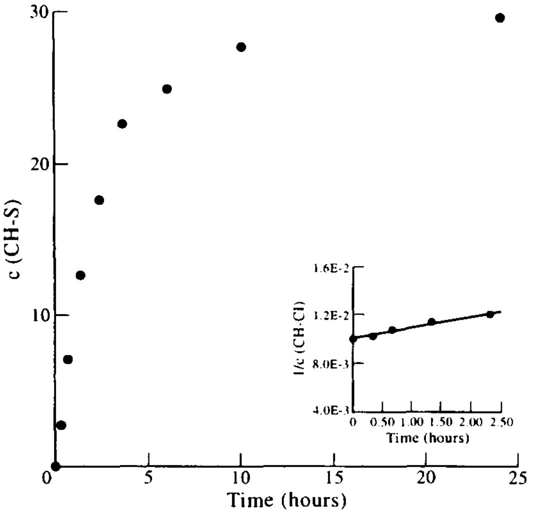

Figure 3 Reaction kinetics of PVC modification with 4-aminothiophenol in cyclohexanone at 60°C. Inset: determination of the reaction order

of amino peaks (3200–3500 cm^{-1}) to C–H valence peaks (2850–3100 cm^{-1}) plotted as a function of the molar composition of the respective mixture.

The results obtained from the three methods are compared in *Table 1*. Within the experimental error a good agreement between the data is observed.

In *Figure 3* the degree of modification of PVC is shown as a function of the reaction time. At the beginning the reaction is very fast. After about 12 h the equilibrium state is reached, at a maximum conversion of 30%. As shown in the inset of the figure, this reaction is of second order, which is expected for nucleophilic substitution under the given conditions. These results are in good agreement with the kinetics measured for PVC modifications with similar compounds.

Thermal properties. Calorimetric measurements were performed in order to analyse the thermal properties of the modified PVCs and the influence of the amino groups on T_g. In *Figure 4* the T_g dependence is plotted as a function of the degree of modification of PVC. It can be seen that T_g values increase linearly with conversion. An opposite behaviour had been observed for PVC modified with thiophenol. In the polymer containing amino groups the higher T_g can be explained by chain–chain interactions via hydrogen bonds.

The change of T_g in copolymers as a function of the molar composition follows a linear relationship as described by the Flory–Fox equation for random copolymers. Using this equation a theoretical value of 156°C is deduced for the totally transformed PVC.

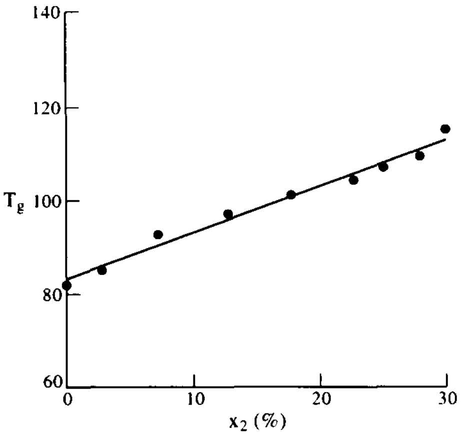

Figure 4 Glass transition temperatures T_g of PVC-NH$_2$ as a function of the degree of modification

Applications of PVC-NH$_2$. The introduction of amino groups into the PVC backbone opens a wide field of applications due to the high reactivity of the amino groups towards acid chlorides.

As an example, the synthesis of PVC with a covalently bound plasticizer was undertaken. *Figure 5* shows the n.m.r. spectrum of PVC-NH$_2$ (modification degree 6%) after the reaction with an excess of dodecanoylchloride. The peak of the amino groups at 5.2 ppm has disappeared completely. Instead there is a new peak at 10 ppm, indicating the formation of an amide proton. In the same way the amino group can be used to graft other kinds of agent to the PVC chains, producing polymers with covalently bound dyes or u.v. stabilizers. It is also possible to introduce specific groups to PVC and thus change its solubility characteristics.

When PVC-NH$_2$ is reacted with diacid chlorides, cross-linked PVC can be obtained. Thin films (150 μm) were produced by spin-casting, and immersed at 0°C in a THF solution which contained adipoyl dichloride. Cross-linking takes place instantaneously, and the films do not dissolve but swell instead according to the number of amino groups in the PVC.

Measurements of the mechanical properties of these cross-linked products will be reported elsewhere[16].

Conclusions

It has been shown that *p*-aminothiophenol is an appropriate agent to introduce primary amino groups to the PVC backbone. The nucleophilicity of the aromatic thiol group under the chosen reaction conditions is far higher than that of the amino group, so that selective modification takes place and cross-linked side-products are not obtained even at high modification degrees. The presence of amino groups in PVC changes markedly the chemical and physical properties of the system. The high reactivity towards acid chlorides can be used to introduce easily covalent-bound additives to PVC. Furthermore, the increase of chain–chain interactions by hydrogen bonds is liable to improve the mechanical properties of polymer films. Amino group-containing polymers are also interesting as fixed-site proton carrier membranes. A corresponding study of aminated PVC is now in progress.

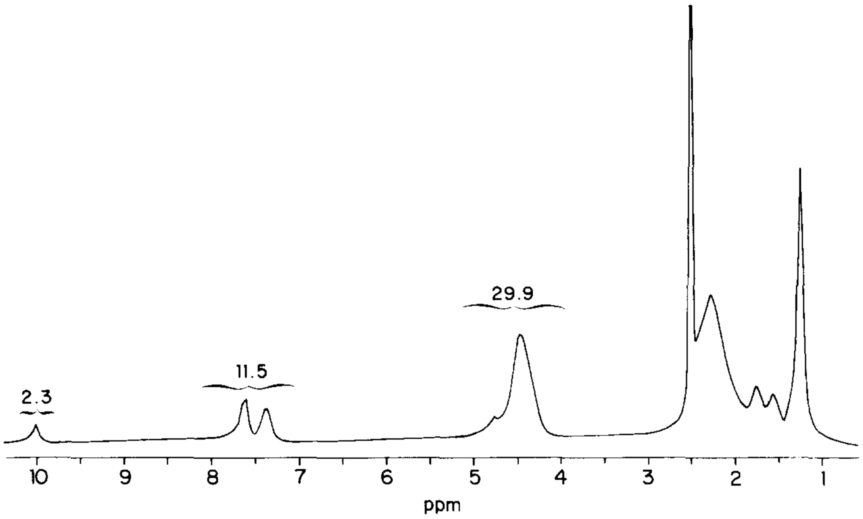

Figure 5 N.m.r. spectrum of PVC-NH_2 after modification with dodecanoyl chloride

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