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Vinylamine polymer via chemical modification of PVC

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Abstract

Chemical modification of PVC using $NaNO_2$ in THF/DMSO(1:1) or DMF/DMSO(1:1) solutions has been achieved without appreciable discolouration. Transformation yields as high as 73% have been attained at room temperature with long reaction times. The modified polymer is not explosive under the conditions studied and has a C=C unsaturation content of less than 10%. Interestingly, GPC analysis indicates that appreciable chain scission occurs and typically the molecular weight is reduced from 73700 to 12000 during chemical modification. Reduction of the resulting polymer with hydrazine hydrate in the presence of Pd(10%)–C catalyst gives a water-soluble vinylamine-derived polymer. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer modification; Modification of PVC; Modification with sodium nitrite; Vinylamine polymer

1. Introduction

Although PVC is one of the most abundant synthetic polymers it differs from its low molecular weight alkyl halide analogues in that it does not readily undergo simple nucleophilic substitution reactions. Instead dehydrochlorination is favoured under many conditions of condensation reactions and consecutive double bond formation occurs to yield dark coloured products [1].

Nucleophilic substitution with thiols and thioethers has been reported to be successful to some extent [2,3]. Modification using dithiocarbamates [4], NaN_3 [5] and $Na_2S_2O_3$ yielding the corresponding Bunte Salt [6] have also been demonstrated to be successful.

In the present communication, we show that reaction of PVC with $NaNO_2$ in THF/DMSO mixtures gives a yellow-brown nitrated product which is soluble in ethyl acetate, DMF, NMP but insoluble in toluene. Catalytic reduction of this using Pd(10%)–C catalyst with hydrazine hydrate in 2-butoxy ethanol (butyl cellosolve) affords a water-soluble polyamine. As far as we know, there appears no report in the literature on the modification of PVC using sodium nitrite, possibly because of the potentially explosive nature of this polymer.

2. Experimental

All the chemicals used were analytical grade commercial products. They were used as supplied; PVC (Aldrich, high molecular weight), THF (E. Merck), DMSO (Aldrich), Pd catalyst (Pd(10%)–C Merck), $NaNO_2$ (Merck), hydrazinium hydroxide (100%, Merck).

2.1. Modification of PVC using $NaNO_2$

$NaNO_2$ (10 g, 0.145 mol) was dissolved in DMSO (25 ml) at room temperature. This solution was added dropwise to a stirred solution of PVC (6.25 g, 0.10 mol Cl) in THF (40 ml). Some flocculation was observed at the beginning of the process. These flakes became

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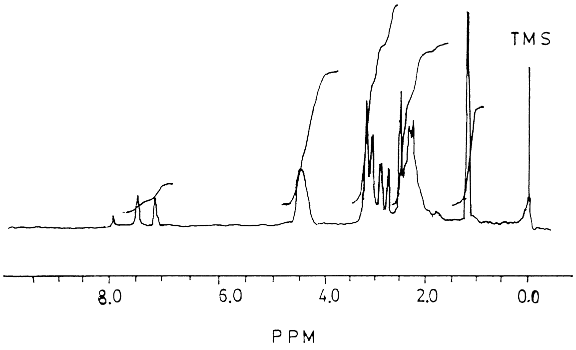


Fig. 1. ^{1}H-NMR spectrum of polymer (**2**).

dispersed after ~1 h of mixing. Then the clear solution gradually became cloudy due to precipitation of NaCl.

Stirring was continued for 24 h and the mixture turned light brown in colour. Then the reaction mixture was heated at 60°C for 1 h and poured into water (250 ml). NaCl (7 g) was added to settle the product. This was filtered off, washed with excess of water and dried at room temperature under vacuo for 24 h. Yield of polymer (**2**) 6.2 g. The ^{1}H-NMR spectrum of the compound (in DMSO$_{d\text{-}6}$, TMS as internal standard) is given in Fig. 1. Polymer (**2**) is soluble in ethyl acetate, DMSO, DMF, and 2-butoxy ethanol; slightly soluble in ethanol, methanol and acetone, and insoluble in water.

2.2. Catalytic reduction of polymer (2)

Polymer (**2**) (4.8 g) was dissolved in 2-butoxy ethanol (30 ml) in a 250 ml two-necked flask fitted with a reflux condenser and a dropping funnel. Pd(10%)–C catalyst (0.2 g) was added to the mixture with stirring. Then hydrazinium hydroxide (15 ml) was added through the funnel and the mixture stirred and heated at 80°C for 24 h. After cooling, the reaction mixture was poured into distilled water (200 ml) and filtered. The filtrate was evaporated to a volume of ~10 ml. The solution was transferred to a rotary evaporator and the residual solvent was removed. The residue was dissolved in methanol (30 ml) and poured into diethyl ether (100 ml). The precipitate was collected and dried under vacuo at 45°C for 24 h. Yield of polymer (**3**) 2.9 g. Polymer (**3**) is soluble in water, ethanol, DMSO and $CHCl_3$. Its ^{1}H-NMR spectrum is given in Fig. 2.

Alternatively, polymer (**3**) was obtained in its HCl form by adding concentrated HCl solution (5 ml) to the initial residue dissolved in ethanol (20 ml). The HCl form of polymer (**3**) precipitated was collected by filtration and washed with ethanol (~10 ml) and ether (~10 ml). Then it was dried at 40°C under vacuo for 24 h. The dry polymer weighed 1.6 g.

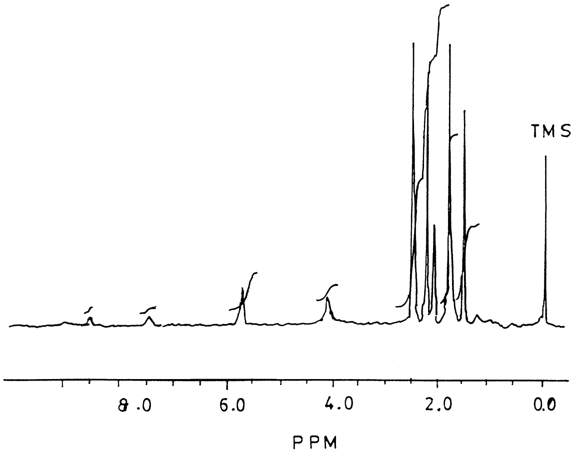


Fig. 2. ^{1}H-NMR spectrum of polymer (**3**).

2.3. Determination of the chlorine content of polymers

Polymer (**2**) (0.3 g) was ground up and mixed with NaOH–K_2CO_3 (1:1) (6 g) in a porcelain pot and fused by means of a bunsen burner. After cooling, the mixture was dissolved in distilled water (30 ml), filtered and the pot washed with water. The filtrate and washings were combined and made up to 100 ml in a volumetric flask. The chlorine content was determined by the silver chloride precipitation method as described in the literature [8]. The residual chlorine content of polymer (**2**) was found to be 2.44 mmol g^{-1} corresponding to ~16.0% of segments. Similar analysis of polymer (**3**) gives 11.8% chlorine content.

2.4. Determination of the nitrite ester content of polymer (2)

The nitrite ester content was determined by a modified Libermann method as follows.

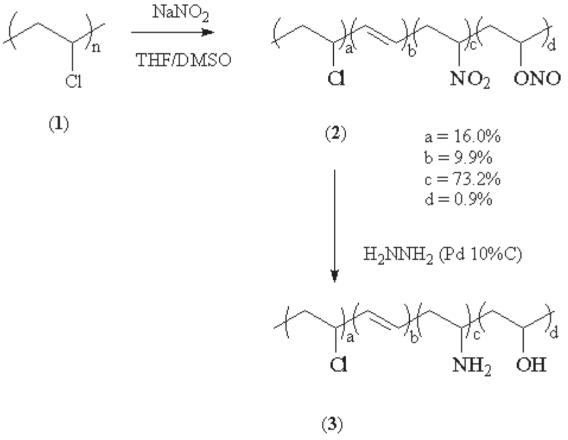
Polymer (**2**) (50 mg) was dissolved in DMF (5 ml). A solution of 2,7-dihydroxy napthalene (1 g) in ethanol (45 ml) was mixed with concentrated HCl solution (5 ml). To 5 ml of this mixture was added 1 ml of the polymer solution in DMF. The nitrite content was assayed based on the absorbance maxima at 440 nm, as described in the literature [9]. The nitrite ester content of polymer (**2**) was found to be 0.145 mmol g^{-1} corresponding to ~0.9% of segments.

2.5. Determination of the amine content of polymer (3)

The amine content of polymer (**3**) was determined by the Van Slyke method as described in the literature [7].

3. Results and discussion

Reaction of PVC with $NaNO_2$ in a THF–DMSO mixture gives primarily the corresponding nitro derivative in high transformation yield (Scheme 1). The resulting light-brown product (**2**) is soluble in many organic solvents such as 2-butoxy ethanol, ethyl acetate, DMF, DMSO, THF and NMP. PVC itself is not soluble in ethyl acetate and 2-butoxy ethanol. Although the brownish colour of polymer (**2**) might suggest a significant level of conjugated unsaturation in the structure in fact the ^{1}H-NMR spectrum (Fig. 1) indicates only ~9.9% of unsaturation (ratio of the unsaturated proton signals in 5.6–7.5 ppm range to those of saturated protons between 1–4.6 ppm). Although the UV spectrum of polymer (**2**) (Fig. 3) shows a broad absorption between 400–600 nm the observed brown colour may arise from charge transfer interactions. The chlorine analysis indicates the presence of ~16.0% residual vinyl chloride segments in polymer (**2**). Chlorine analysis of polymer (**3**) gives 11.8% chlorine which is somewhat less than that predicted (12.7%) from NMR analysis. This corresponds to 3.32 mmol g^{-1} instead of 3.60 mmol g^{-1} estimated by NMR. The slight difference is in experimental error limits. From the content of C=C, –Cl and –ONO groups the nitro group content corresponds to ~73.2% of segments (Scheme 1).



Scheme 1. Nitration of PVC using $NaNO_2$ and reduction using H_2NNH_2 (Pd(10%)–C).

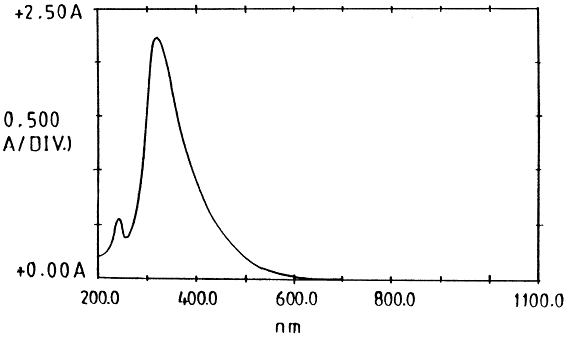


Fig. 3. UV spectra of polymer (**2**).

Catalytic reduction of polymer (**2**) using hydrazine hydrate in 2-butoxy ethanol results in formation of water-soluble polymer (**3**) having similar physical properties to polyvinylamine. Isolation of the free neutral polyamine is difficult but isolation in its HCl form is rather easy.

Transformation of the nitro groups in (**2**) into the amino groups in (**3**) is indicated by comparison of the ^{1}H-NMR spectra in Figs. 1 and 2. The broad signal at 4.18 ppm (in Fig. 1) arises from the the proton on the carbon atom carrying the nitro group along with the proton on the Cl substituted C atom. However, after reduction the former signal disappears almost completely. The residual weak signal intensity of the ($C\underline{H}Cl$) is important evidence of the high conversion in the first reaction step and the efficient reduction of the nitro groups in the second step. Also the sharp signal at around 1 ppm corresponds to the $C\underline{H}_2$ protons between two nitro methyl groups. This resonance disappears completely after reduction.

The classical bromine addition method has not been used for determination of the C=C bond content since bromine substitution at the carbon atom adjacent to the nitro group is a possible side reaction. For this reason the amount of unsaturation was estimated from the ^{1}H-NMR spectra (Figs. 1 and 2).

In the FT-IR spectra of polymer (**2**) (Fig. 4b) and polymer (**3**) (Fig. 4c), no C–H stretching vibration was observed above 3000 cm^{-1} due to the low percentage of the unsaturation. The sharp peak at 1677 cm^{-1} in Fig. 4b seems to be associated with the stretching vibration of the C=C bond. However, in Fig. 4c this band has disappeared almost completely and a broad band arising from N–H plane bending vibration emerges at the same frequency. For this reason the peak at 1677 cm^{-1} cannot be ascribed to the olefinic stretching vibration instead it may be due to the vibration of the nitromethyl groups in (**2**). Another characteristic peak of the nitro group observed at 1350^{-1} in Fig. 4b, disappears in polymer (**3**) (Fig. 4c). This is a clear evidence for reduction of the nitro groups. Also the broad band in the 3200–3500 cm^{-1} range in Fig. 4c can be attributed to the N–H stretching vibrations of the amino groups in (**3**).

It is important to note that, GPC analysis of the modified polymer (**2**) (Fig. 5) shows a sharp decrease in the molecular weight in relation to that of the starting PVC. Also comparison of the inherent viscosities of PVC and polymers (**2**) and (**3**) shows a marked decrease consistent with chain scission (Table 1) during modification with $NaNO_2$. At the moment it is not possible to

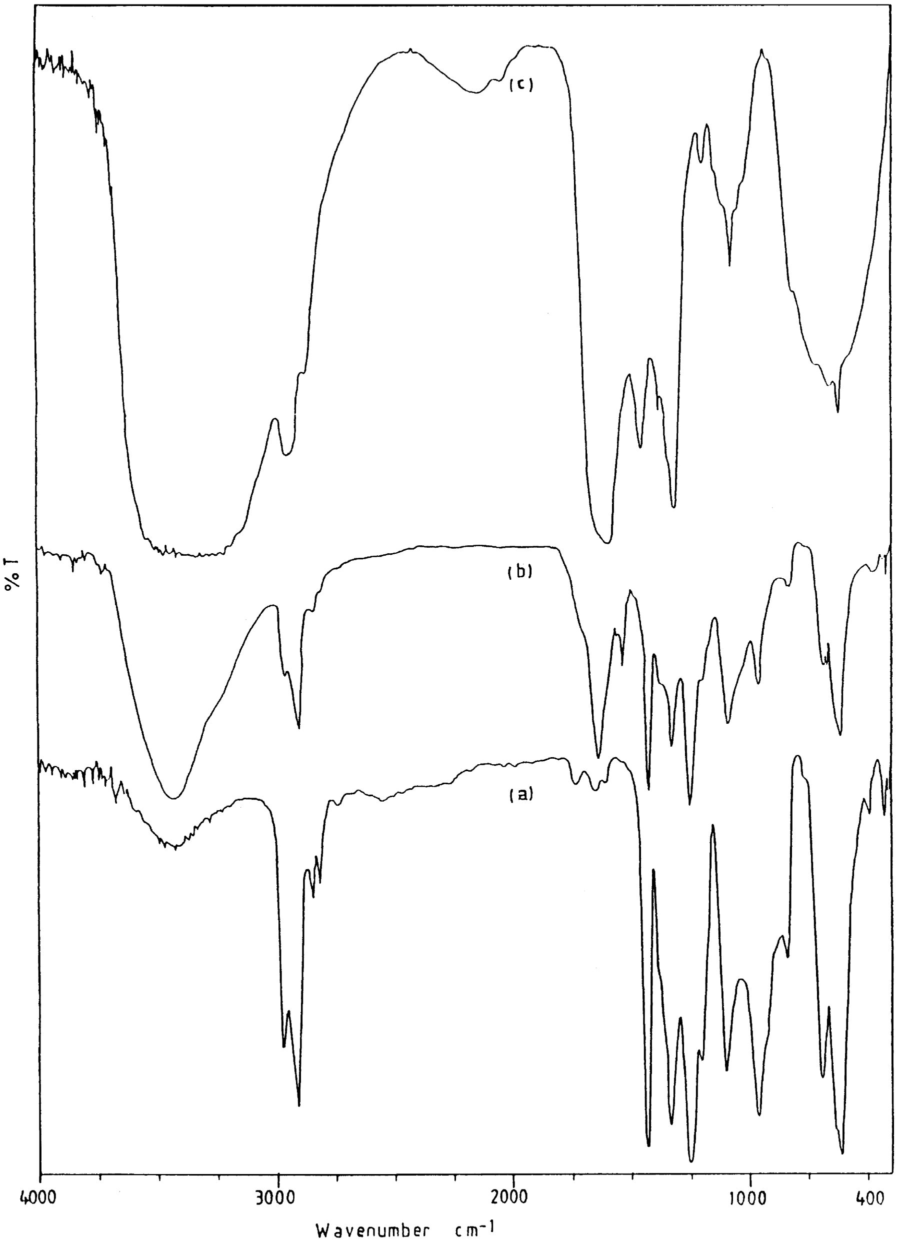


Fig. 4. FT-IR spectra of (a) PVC, (b) polymer (**2**) and (c) polymer (**3**).

suggest a mechanism for this process which appears to take place under very mild conditions. Further work is necessary to shed light on this.

Although an extensive systematic study targeted towards optimisation of these reactions involving PVC has not been completed it has been found that if THF is replaced with DMF the reaction with $NaNO_2$ does not proceed at room temperature and formation of a marked deep coloured product is observed at 60–70°C. Clearly, therefore, the nitration reaction is very solvent dependent. It also seems unlikely that the mechanism involves direct substitution of $-Cl$ by $-NO_2$. A more likely possibility involves loss of HCl and addition of NO_2 to the so-formed C=C. Because in all reactions of PVC dehydrochlorination is major reaction in various solvents, due to well-known unzipping mechanism. For instance according to our own experience modification with thiolates leads to discolourations when stoichiometrical amounts are used. High substitutions can be attained in presence of excess of thiolates. This obser-

Table 1
Some characteristics of PVC and its chemically modified derivatives (**2**) and (**3**)

Polymer	Molecular weight[a] (M_n)	Inherent viscosity[b] (dl g^{-1})	Colour	Chlorine content (mmol g^{-1})	Nitrite ester content (mmol g^{-1})
PVC	73,700 $M_w/M_n = 1.22$	0.73	White	nd[c]	–
(**2**)	12,000 $M_w/M_n = 1.63$	0.33	Light brown	2.44	0.145
(**3**)	nd	0.24	Yellow	3.32	0.0

[a] By GPC with polystyrene standard.
[b] In DMF (1 dl g^{-1}, at 25°C) using Ubbelohde viscometer.
[c] nd not determined.

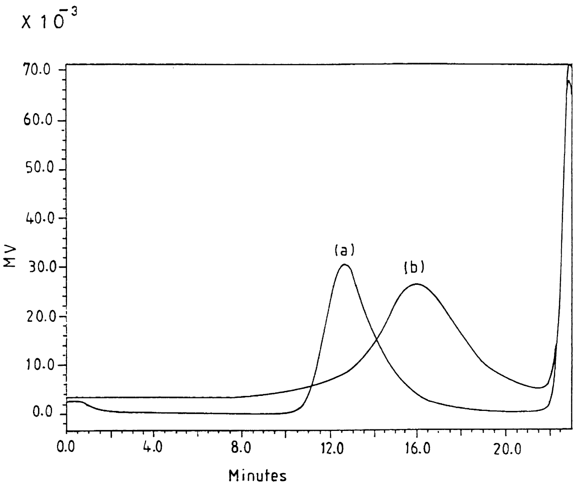


Fig. 5. GPC elution profiles of (a) PVC and (b) polymer (**2**).

vation supports the two step mechanism. Also addition of nitrogen oxides to olephinic double bonds is one of the method to prepare aliphatic nitro compounds. This fact is in accordance with the above consideration.

Moreover, nitrite ester formation is another side reaction yielding 0.145 mmol g^{-1} of these groups in polymer (**2**). The nitrite ester groups are expected to hydrolyse under the conditions of reduction and work-up of polymer (**3**), and repeating the nitrite ester test on this polymer indeed gave a negative result.

In conclusion, this study reveals that

1. PVC can be chemically modified using sodium nitrite without appreciable dehydrochlorination.
2. The conversion to nitrated product is high (~75% segments).
3. The reaction proceeds with simultaneous chain scission yielding a significant drop in polymer molecular weight.
4. Formation of a nitrite ester by-product during the modification is minor.
5. Somewhat contrary to expectation, the nitrated polymer is not explosive under ambient conditions. A moderate explosion is observed when the dry sample is deliberately put on a hot plate.
6. Reduction of the nitrated polymer to the corresponding amino derivative i.e. to a poly(vinylamine) can be achieved readily and cleanly.
7. The mechanism of the nitration reaction is not known, but almost certainly does not involve direct substitution of –Cl by –NO_2. Loss of HCl and addition of NO_2 to the so-formed C=C seems more likely.

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