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polymer

PVC containing hydroxyl groups
I. Synthesis, characterization, properties and crosslinking

Manuel Hidalgo, Helmut Reinecke, Carmen Mijangos*

Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain

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Abstract

A detailed characterization of hydroxylated poly(vinyl chloride) (PVC), obtained by modification of PVC with *p*-mercaptobenzyl alcohol and its crosslinked homologues, is described. The selective character of the modification with respect to the thiol group and the presence of free hydroxyl groups in the polymer is shown using ^{1}H-NMR. The stereoselectivity of the reaction is provided from ^{13}C-NMR. The presence of physical interactions in the system by hydrogen bonding is deduced from light scattering measurements and analysis of the thermal and mechanical properties. The critical concentration of hydroxyl groups required in the chains in order to form an efficient physical network is determined to be about 4%. Chemical networks are obtained by reaction of hexamethylene diisocyanate with the hydroxyl groups present in the polymer, and the process is followed by IR spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl chloride) modification; Hydroxylated poly(vinyl chloride); Poly(vinyl chloride) crosslinking

1. Introduction

The introduction of hydrophilic groups into commodity polymers provides new applications as functions of the modification of the physical or chemical properties of the polymer. Thus, increasing the polarity and the intermolecular forces, variations in solubility characteristics, grafting of additives into the chain and the generation of adjustable networks by crosslinking reactions are some of the macroscopic changes expected.

The functionalization of polyolefins with maleates, maleic acid, acrylic acid and others, has been widely reported in the literature [1–14], and demonstrates the existence of a plateau in the reaction kinetics at low degrees of conversion. On the contrary, for poly(vinyl chloride) (PVC), it is well known that, up to high conversions, thioaromatic compounds can easily selectively substitute the chlorine atoms of the polymer chain, without secondary reactions, and under a wide range of reaction conditions: solution, aqueous suspension or in melts [15–27].

Consequently, in the case of PVC, it is possible to introduce hydrophilic groups in the chain by performing substitution reactions on the polymer with difunctional thioderivates as carriers of these groups. Unfortunately, such a selective reagent does not exist commercially. In a preliminary study, we reported the synthesis of two reagents, 2-mercaptobenzyl alcohol and 4-mercaptobenzyl alcohol, and their potential application in the production of hydroxylated PVC which, by reaction with a diisocyanate, can be partially crosslinked in a second step [28]. Nevertheless, a detailed description of the substitution kinetics, micro- and macrostructural characterization of the modified polymer and its crosslinking has not been reported. In this work, we report an extensive study of the synthesis, characterization, properties and crosslinking of hydroxylated PVC.

2. Experimental

2.1. Substitution reaction on PVC

Commercial bulk polymerized PVC was obtained from ELF ATOCHEM (Spain), with a weight-average molecular weight, $\bar{M}_w = 58\,000$. The tacticity, measured by ^{13}C-NMR, was syndiotactic = 30.6%, heterotactic = 49.8% and isotactic = 19.6%.

The synthesis of 4-mercaptobenzyl alcohol and the nucleophilic substitution reaction on PVC in solution were described in a previous paper [28]. Different reaction conditions were employed in order to optimize the modification process as a function of the solvent, temperature and the concentration of reagent.

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* Corresponding author.

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2.2. Chemical composition and microstructure

The chemical composition of the modified polymers was determined by ^{1}H-NMR spectroscopy. Spectra were recorded at 25°C from 5% solutions in deuterated dimethyl sulphoxide on a 200-MHz Varian XL spectrometer operating at 200 MHz, by means of the ratio of the band areas corresponding with modified and unmodified polymer triads.

The stereochemical structure of the modified polymers was determined by ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectra were recorded at 90°C from solutions in deuterated dimethyl sulphoxide on a 300-MHz Varian XL spectrometer operating at 75.5 MHz, under conditions described elsewhere [20,29]. The resonances used were those of the methine carbons of the backbone, ranging from 57 to 62 ppm for the modified polymer. The calculations were carried out by measuring the relative areas of the different peaks with a compensating polar planimeter.

2.3. Average molecular weight

Light scattering experiments were performed on a Wyatt Dawn-F apparatus measuring the scattering of six concentrations from the respective polymers in tetrahydrofuran (THF). The weight-average molecular weights were evaluated from classical Zimm diagrams. The refractive index increments (dn/dc) were determined on a KMX-16 differential refractometer at a wavelength of $\lambda = 632.8$ nm.

2.4. Differential scanning calorimetry

The calorimetric measurements of the modified PVCs were carried out using a Perkin Elmer DSC-7. Thermograms were recorded between 40°C and 150°C at a heating rate of 10°C/min. The T_g values were taken from the midpoint of the transitions in the second scan.

2.5. Mechanical properties

The stress–strain behaviour of the modified PVCs was studied on a temperature-controlled Instron 4031 universal dynamometer. The measurements were performed at 90°C, using a 0.1 kN load cell and with a testing speed of 50 mm/min. Samples were prepared from films of 40–45 μm thickness, cast from THF solutions. After Soxhlet extraction in diethyl ether, dumbbell-type samples of 2 mm width at the deformation zone were cut. From each polymer sample, a minimum of four samples were tested.

2.6. Crosslinking reaction

Solutions of copolymer in dry THF (50 mg/ml) and a half molar amount (with respect to the number of hydroxyl groups) of hexamethylene diisocyanate (HMDI) were prepared in 5-ml hermetically sealed glass flasks and thermostatted at 60°C with stirring for 1 h. The homogeneous viscous solution was then placed on a glass plate and the solvent evaporated under a slow stream of dry N_2. Crosslinking of the films was carried out in a vacuum oven at 60°C for a period of 8 h. Purification of the networks obtained was achieved by extraction with THF (24 h) and diethyl ether (24 h) in a Soxhlet apparatus.

In this study, networks of varying crosslink density and number of free hydroxyl groups were investigated. The latter systems were synthesized using less than the stoichometric amount of NCO groups.

2.7. Crosslinking kinetics

Crosslinking of modified PVC was followed by IR spectroscopy on a Nicolet 520 IR-FT spectrometer by recording the IR spectrum at different time intervals during the crosslinking of unextracted 15- to 40-μm-thick films, prepared as described above.

The degree of conversion of the crosslinking reaction was determined using the method described by Hensema and Berger [30]. The construction of a calibration curve, where the ratio of the 2277 cm^{-1}/2990 cm^{-1} band areas is plotted against the molar concentration (percentage of NCO groups), allows one to obtain the concentration of unreacted diisocyanate.

3. Results and discussion

3.1. Chemical constitution of the modified PVC

The modification reaction is performed under different conditions, as indicated in the Experimental section. Samples were withdrawn at different time intervals. After precipitation and purification, they were analysed by ^{1}H-NMR spectroscopy.

In Fig. 1, the corresponding spectra of the PVC for different degrees of modifications are shown. With increasing reaction time, aromatic (7.3 ppm) as well as hydroxyl proton peaks (5.3 ppm) are observed. Benzyl proton peaks increasing at 4.5 ppm are overlapped by the signal of the CH–Cl protons. The latter decreases with conversion, whilst two new peaks at 4.8 and 3.3 ppm are formed due to CH–Cl (with a CH–S unit in the neighbourhood) and CH–S protons, respectively. The signal at 3.3 ppm is partially covered by the H_2O peak. The degree of modification, $MD(\%)$, can be calculated from the NMR spectra using the formula:

$$MD(\%) = \frac{S(\mathrm{C}H\mathrm{OH})}{S_{\mathrm{Corr}}(\mathrm{C}H\mathrm{Cl}) + S(\mathrm{C}H\mathrm{OH})} \times 100,$$

where S are the areas of the respective proton signals, obtained from:

$$S(\mathrm{C}H\mathrm{OH}) = S(\mathrm{CH_2O}H) = 1/4 S(\mathrm{C}H_{\mathrm{Ar}})$$

$$S_{\mathrm{Corr}}(\mathrm{C}H\mathrm{Cl}) = S(\mathrm{C}H\mathrm{Cl}) - 2S(\mathrm{C}H_2\mathrm{OH})$$

$$= S(\mathrm{C}H\mathrm{Cl}) - S(\mathrm{CH_2O}H).$$

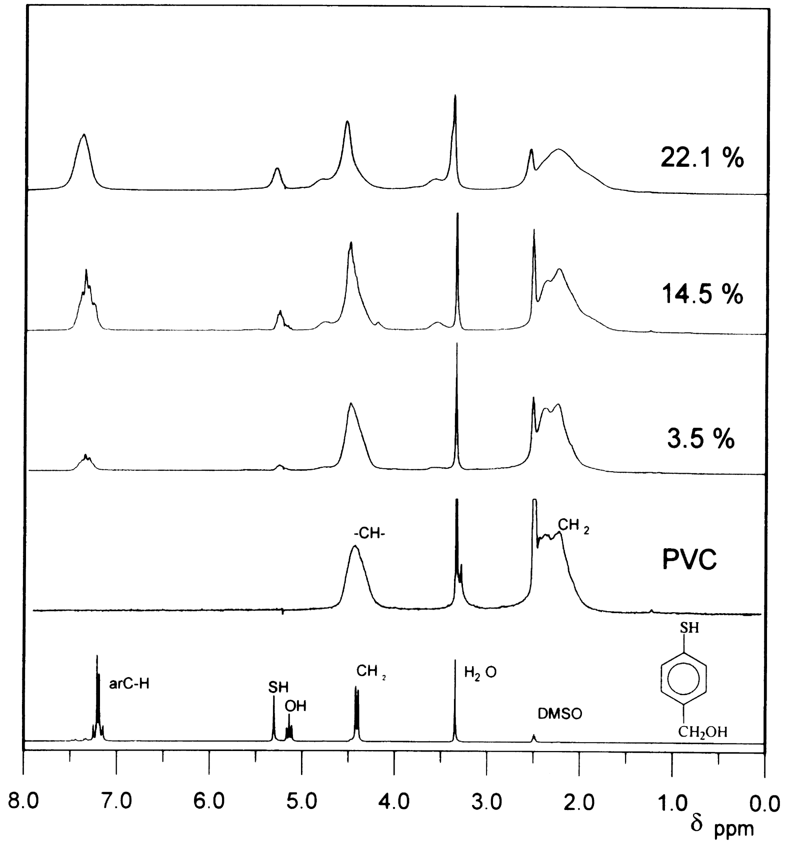


Fig. 1. ^{1}H-NMR spectra of different PVCs modified with 4-mercaptobenzyl alcohol, raw polymer and reagent.

The band corresponding to the CH_2OH protons is completely overlapped by the CHCl signal. Thus, in order to determine the real value of S(CHCl), designated as S_{Corr}(CHCl), it is necessary to subtract the above-mentioned band.

Analysis of the NMR data reveals some important features of this modification reaction. 4-Mercaptobenzyl alcohol is a suitable agent for the obtention of PVC with free hydroxyl groups, indicated by the NMR peak at 5.3 ppm. The nucleophilic substitution reaction is completely selective with respect to the mercapto group, indicated by the fact that the ratio of aromatic to hydroxyl proton peaks is 4:1, independent of the conversion. This modification reaction is free of undesired side reactions such as elimination or crosslinking. Thus, white THF-soluble products are obtained.

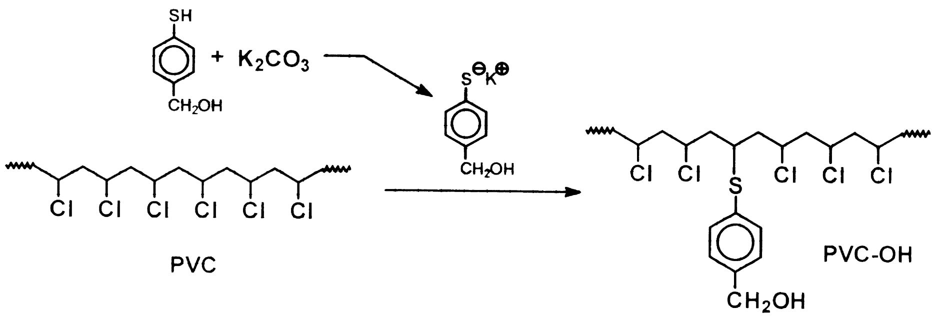
A detailed analysis of NMR data of PVC reduced or substituted with many thio derivatives has been reported elsewhere [16,20,21,29]. It has been found that the evolution of the different compositional triads with molar composition corresponds to a random substitution for all substituted polymers.

3.2. Modification kinetics

Based on previous work [28], the modification of PVC with 4-mercaptobenzyl alcohol was studied as a function of different reaction conditions, such as temperature, solvent and reagent concentration, in order to optimize the reaction, leading to a fast and controlled process without any secondary reactions. The modification reaction is shown in Scheme 1.

In Fig. 2, the most relevant results of this study are shown. The existence of a fast first step followed by a second slower one can be observed in all cases. This behaviour has been widely explained in previous works [15–26] and is typical of PVC modification with aromatic thiols. Comparing runs (a) and (b), it can be deduced that by increasing the solvent polarity the reaction rate is increased and higher degrees of modification are obtained. This is explained by the larger solubility of CO_3K_2 and potassium thiolate as the solvent polarity is increased. On the other hand, comparing runs (b) and (d), it can be observed that the reaction rate is independent of thiol concentration, but most of the reactive chlorine atoms in the polymer are equivalent in both runs.

Finally, run (b) was selected in order to prepare the majority of the modified PVCs, because it allows us to obtain degrees of conversion up to 20% in short reaction times, under gentle reaction conditions and with significant savings in reagent use.



Scheme 1.

3.3. Stereochemical structure

In Fig. 3, the evolution of the ^{13}C-NMR spectra of PVC with increasing degrees of modification is shown. The determination of the configurational monomer sequences in the polymer were based on calculations from the following assignment of the signals. In unmodified PVC, the regions at 47.0–49.5 and 57.3–59.7 ppm represent the methylene and the methine carbons, respectively. The methine carbon region consists of three well-separated main peaks centred at 57.5 (C_1), 58.5 (C_2) and 59.3 ppm (C_3), corresponding to isotactic, heterotactic and syndiotactic triads. This fact has been applied very successfully for the determination of configurational monomer sequences in the polymer [20]. In the figure, it can be observed that upon modification new bands appear at 60.1 ppm (C_4) and for higher conversions at 61.5 (C_5) and 59.0 ppm (C_x; where it is partially overlapped by C_3). Also, in the methylene carbon region (44.0–49.0 ppm), the appearance of new signals can be observed.

A detailed NMR analysis carried out by Mijangos and López [20] of vinyl chloride–vinylthiobenzene copolymers—the structure of which is supposedly very similar to that of the system presented in this paper—was performed using two-dimensional inverse heteronuclear ^{13}C–^{1}H correlation spectroscopy. According to this investigation, the new signals found between 60.0 and 62.0 ppm can be assigned to the methine carbons CHCl of the ClClS (~ 60.0 ppm) and SClS (~ 61.5 ppm) triads, respectively, and the signal at 59.0 ppm to ClClS triads, situated between methine carbons of syndiotactic CHCl regions. The signals in the methylene carbon region, on the other hand, were found to correspond to methine carbons (46.0–47.0 ppm) and methylene carbons (45.5–44.0 ppm) of XSX triads (with X = S, Cl).

The data, summarized in Table 1, show that chlorine substitution takes place mainly in the iso- and heterotactic sequences, whilst syndiotactic regions remain almost unaffected by the reaction. These results have also been found in previous works on PVC modified with thiophenol and *p*-thiocresol [19–21].

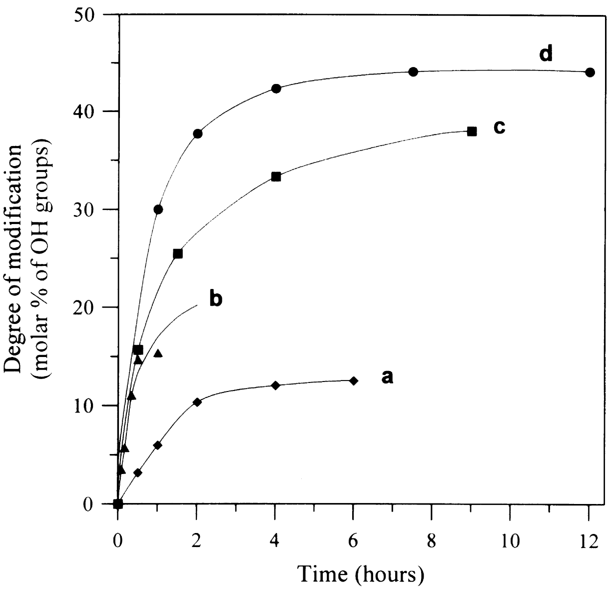


Fig. 2. Modification kinetics of PVC with 4-mercaptobenzyl alcohol. (a) Cyclohexanone at 45°C (◆), [thiol]/[PVC] = 0.5. (b) Dimethylformamide at 45°C (△), [thiol]/[PVC] = 0.5. (c) Cyclohexanone at 60°C (■), [thiol]/[PVC] = 1. (d) Dimethylformamide at 45°C (●), [thiol]/[PVC] = 1.

3.4. Molecular weight

In order to ensure that no polymer degradation takes place during the modification reaction, the weight-average molecular weight of the polymers was determined by means of light scattering experiments. $\bar{M}_w$ values were calculated from the respective Zimm diagrams for the polymers. The results are presented in Fig. 4 as a function of the degree of modification of PVC. At low conversions, up to around 5%, the measured weight-average molecular weights correspond to those expected theoretically. However, for higher conversions a strong deviation from the theoretical curve is observed, and much higher values than those calculated were obtained. In previous studies on PVC modified with β-thiophenol or *p*-thiocresol, reagents with an analogous chemical structure to that of 4-mercaptobenzyl alcohol, it has been shown that the nucleophilic substitution reaction

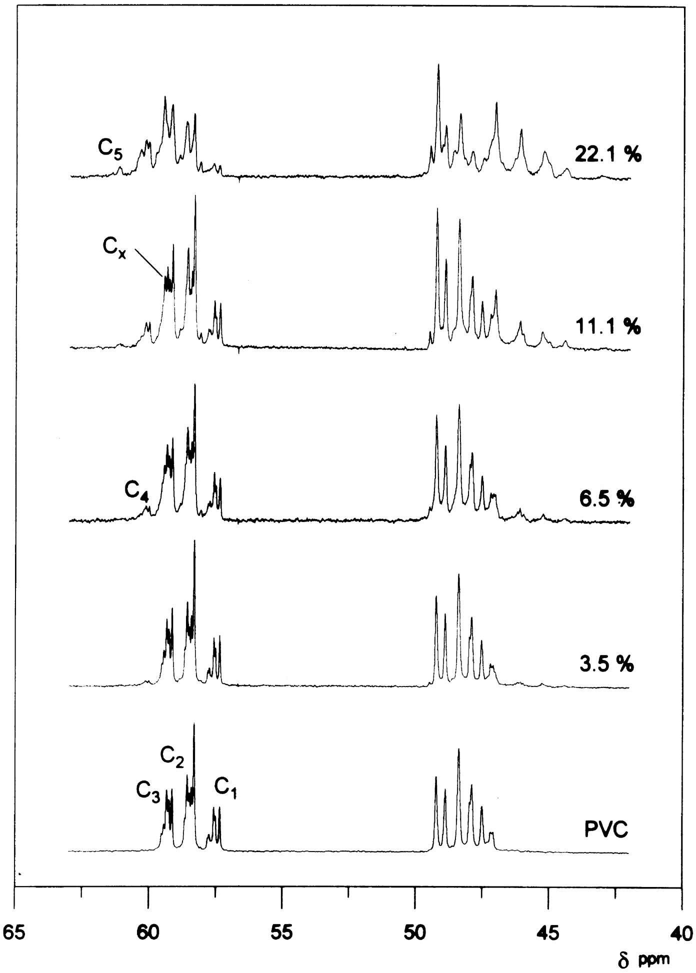


Fig. 3. ^{13}C-NMR spectra of different PVCs modified with 4-mercaptobenzyl alcohol and raw polymer.

with this type of compound is free from side reactions such as elimination, degradation or crosslinking, and that in these cases the experimentally obtained molecular weights correspond to the theoretical curve [19–21].

The polymers modified with 4-mercaptobenzyl alcohol have been shown to be white and THF-soluble, thus implying that neither elimination nor crosslinking had taken place during the modification. Therefore, the strong increase of the mean weight-average molecular weights with conversion must have its origin in the presence of polymer aggregates formed by hydrogen bond interactions between hydroxyl groups. Accordingly, the calculated values should be considered as apparent molecular weights. Although we have not carried out a specific study of hydrogen bonding in the polymer by IR spectroscopy, because this was not the objective of the work, the unexpected behaviour found in M_w can only be understood by supposing this kind of physical interaction in the polymer. In fact, the only alternative explanation would be chemical crosslinking. This, however, can be excluded as the modified polymer is easily soluble in common solvents and no gelation is observed. Moreover, in the ^{1}H-NMR study performed in deuterated dimethyl sulphoxide, a quantitative amount of hydroxyl groups with respect to the corresponding mercaptobenzyl unit are obtained.

Table 1
Configurational distribution of triads in PVC modified with 4-mercaptobenzyl alcohol, determined by ^{13}C-NMR spectroscopy

	ClClCl		
Degree of modification (%)	Isotactic triads (%)	Heterotatic triads (%)	Syndiotactic triads (%)
0	19.4	49.8	30.6
3.5	17.3	47.5	29.6
6.5	15.0	41.5	27.6
11.1	12.3	38.9	27.6
13.1	11.0	34.3	27.5
22.1	4.9	24.7	28.4

3.5. Thermal behaviour

The study of the thermal properties of the modified PVCs

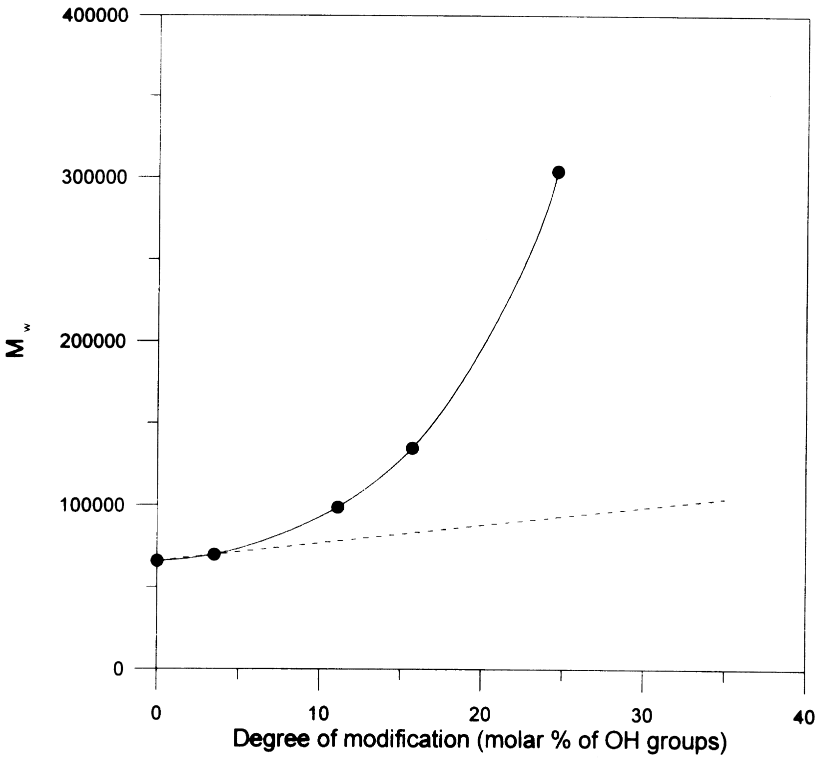


Fig. 4. Evolution of weight-average molecular weight with degree of modification of PVC modified with 4-mercaptobenzyl alcohol. (●) Experimental values; (– – –) theoretical.

was performed by differential scanning calorimetry (DSC) measurements. In all cases, only one glass transition temperature was detected, thus indicating the absence of block copolymer structures. The T_g values obtained from these DSC curves are plotted against the molar conversion in Fig. 5. A decrease of the glass transition temperatures is observed up to conversions of around 5%. A decrease of T_g has also been found for PVC modified with analogous

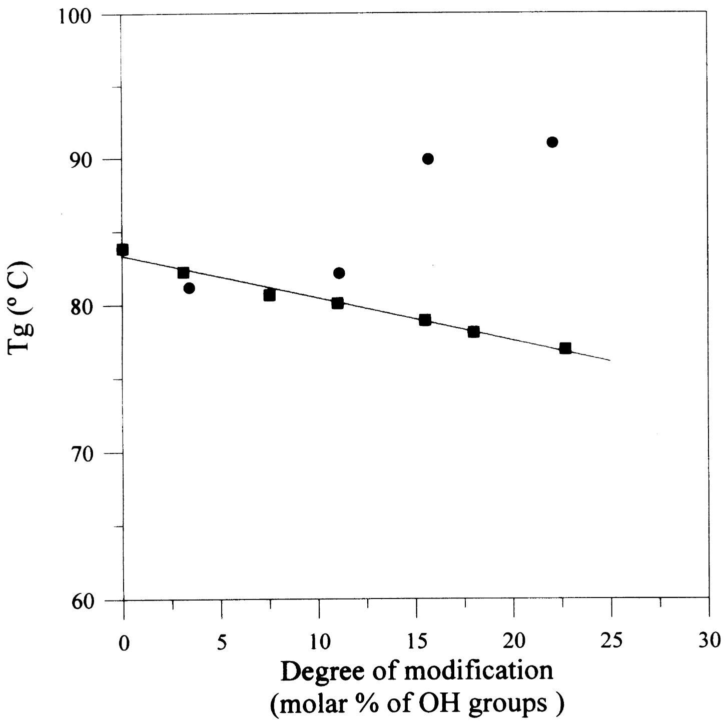


Fig. 5. Evolution of glass transition temperature with degree of modification of PVC. (■) 4-Thiocresol (from Ref. [21]); (●) 4-mercaptobenzyl alcohol.

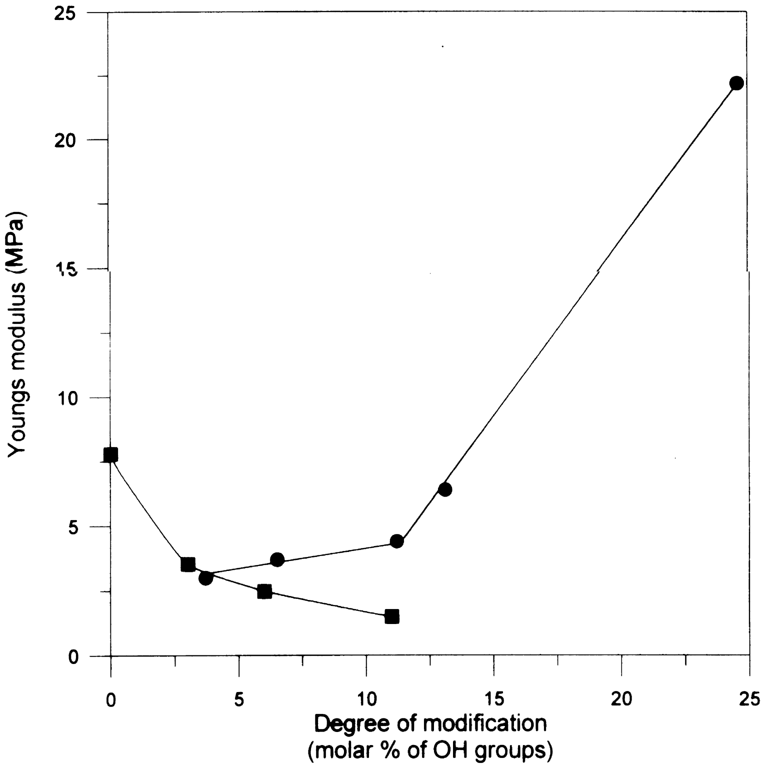


Fig. 6. Dependence of Young's modulus on degree of modification of PVC. (■) 4-Thiocresol; (●) 4-mercaptobenzyl alcohol.

compounds such us thiophenol and *p*-thiocresol, and is due to chain spacing and entropy increases caused by the introduction of bulky molecules to the side chains of the polymer [21].

For PVC with higher degrees of modification, a deviation from the expected behaviour is found and the T_g values increase with conversion. This increase can be explained by the appearance of physical interactions between polymer chains. As explained above, physical interactions due to hydrogen bonding are supposed to occur between the introduced hydroxybenzyl moieties when their concentration in the system is sufficiently high. The existence of hydrogen bonding interactions in the modified PVCs is also reflected in the mechanical properties, as shown below.

3.6. Mechanical properties of hydroxylated PVC

The mechanical properties of PVC modified with 4-mercaptobenzyl alcohol were evaluated from stress–strain curves. The results of this study, shown in Figs. 6 and 7, are compared with the values obtained for PVC modified with 4-thiocresol.

In Fig. 6, the evolution of Young's modulus versus the degree of modification is plotted. The polymer modified with 4-thiocresol shows normal behaviour, i.e. a decrease in the modulus values with the degree of modification, as a consequence of the decrease in the intermolecular interactions due to the introduction of high-volume molecules in the polymer chains.

However, for polymers modified with 4-mercaptobenzyl alcohol, a reagent with an analogous chemical structure to 4-thiocresol (Scheme 2), a significant deviation from the predicted behaviour for degrees of modification above 3–4% is found, leading to an increase in Young's modulus as modification increases. This can be explained by the previously mentioned formation of a physical network by hydrogen bonding interactions between the hydroxyl groups grafted into the polymer.

Suitable results have been obtained from the study of the elongation at break and are given in Fig. 7. The normal plasticizing effect caused by the PVC modification with 4-thiocresol is observed. On the other hand, for hydroxylated PVC, plastification disappears above 3–4% modification and the elongation value decreases as modification increases.

Until now, we have prepared, in a first step, a hydroxylated PVC polymer with a variable but controlled amount of hydroxyl groups, ranging from 0 to 50% or more (depending on the reaction conditions), randomly distributed along the chain, with improved thermal and mechanical properties. This polymer is able to crosslink partially or totally, in a controlled manner in a second step, thus giving rise to an adjustable network, as shown below.

3.7. Kinetics of crosslinking

The crosslinking reaction of hydroxylated PVC and HMDI, as described in the Experimental section, was

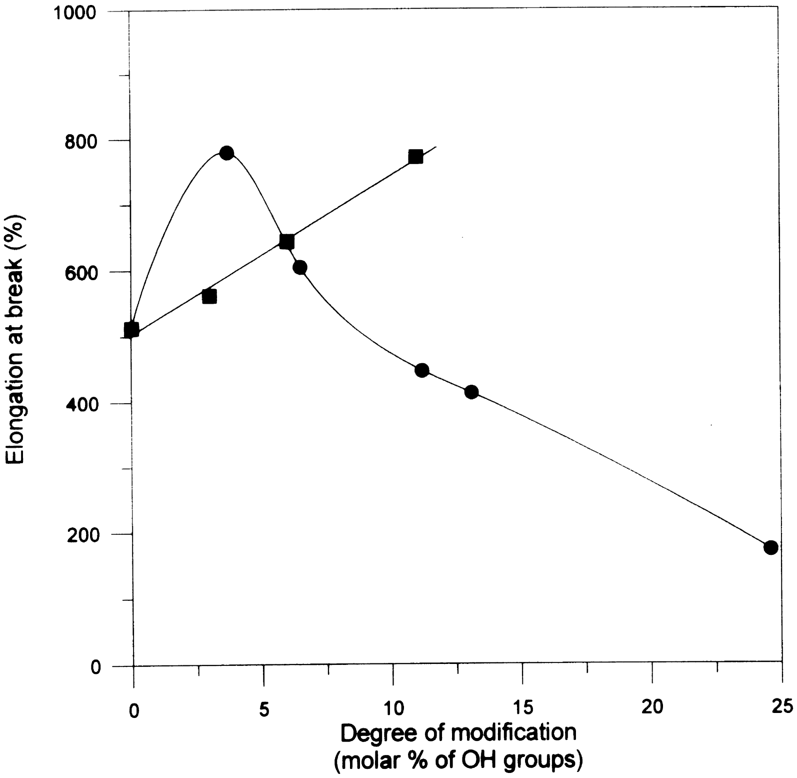
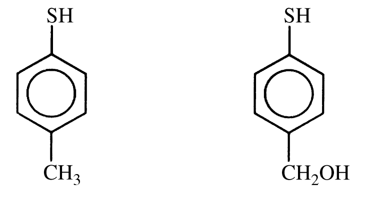


Fig. 7. Dependence of elongation at break modulus on degree of modification of PVC. (■) 4-Thiocresol; (●) 4-mercaptobenzyl alcohol.

studied by IR spectroscopy. In Fig. 8, the evolution of the IR spectra with time during crosslinking is shown. The decrease in the intensity of the band assigned to the isocyanate groups (2277 cm^{-1}, N=C=O, asymmetric stretch) can be observed, as can the subsequent appearance and increase of the amide group bands (1720 cm^{-1}, C=O, stretch, Amide I; 1525 cm^{-1}, NH δ and N–C=O, symmetric stretch, Amide II). Simultaneously, some changes in the 3700–3090 cm^{-1} zone can be appreciated, such as the appearance of a narrow band at 3430 cm^{-1} (N–H stretch free) due to the formation of amide groups and the disappearance of hydroxyl groups during the crosslinking reaction.

As explained in the Experimental section, a calibration curve was constructed in order to determine the number of unreacted NCO groups. Thus, the crosslinking kinetics are expressed as the percentage of reacted NCO groups versus time of reaction. In Fig. 9, the kinetics of crosslinking of a hyroxylated PVC polymer with a degree of modification of 13.2% (molar) in the presence of an equimolar quantity of NCO groups ([NCO] = 2[HMDI]) are plotted. From this figure, it can be deduced that most of the NCO groups react during the solution step and, after the solution casting, the crosslinking is completed in a slower process in the solid state, leading to degrees of conversion of up to 80% in 6 h.



4-thiocresol 4-mercaptobenzylalcohol

Scheme 2.

It can be observed that the selected crosslinking reaction works with an efficiency of almost 100%. This allows us to obtain a huge variety of PVC networks of well-defined dimensions, with a variable and well known number of hydroxyl groups and degrees of crosslinking. The dimensions and properties of the crosslinked polymers will be presented in a further publication [31].

4. Conclusions

Modification of PVC with 4-mercaptobenzyl alcohol in solution is an appropriate process for the generation of hydroxylated PVCs in a selective, fast and controlled manner, without secondary reactions. The characterization of the modified polymers by the determination of the average molecular weight, glass transition temperature and mechanical properties concurs to show the existence of hydrogen bonding interactions, leading to the formation of a physical network in polymers with degrees of modification higher than 3–4%. The hydroxylated PVC can be crosslinked by reaction with diisocyanates. Crosslinking kinetics,

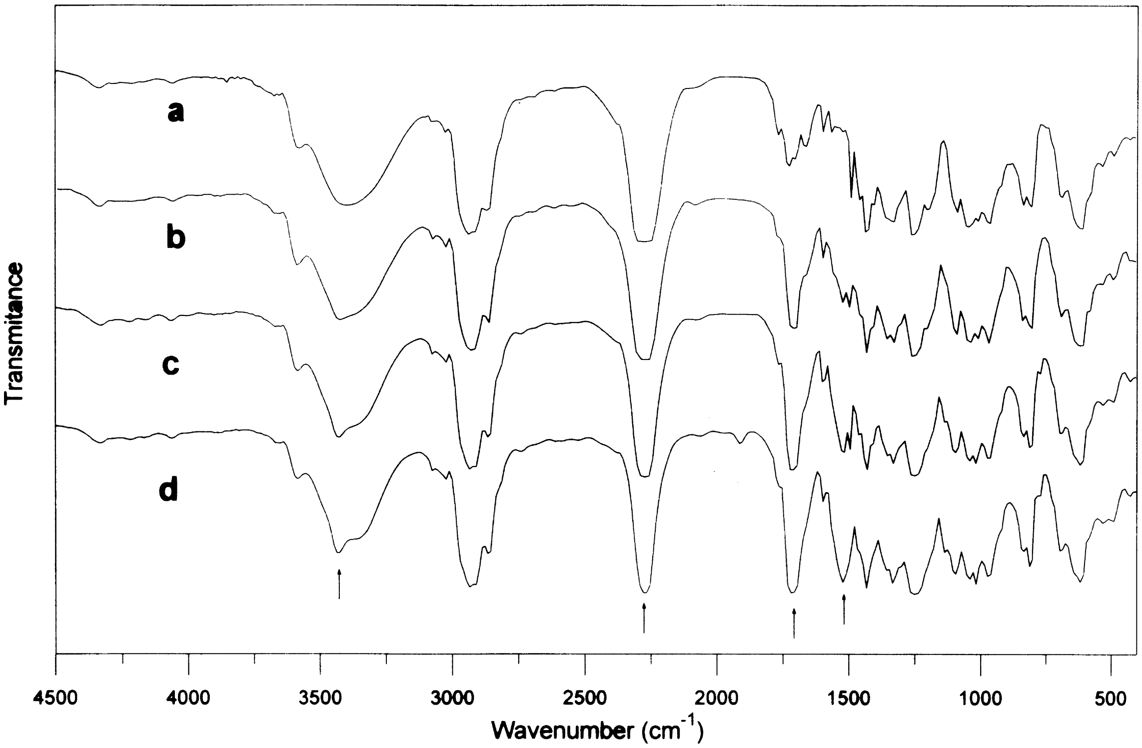


Fig. 8. Evolution of IR spectra of PVC modified with 4-mercaptobenzyl alcohol (13.2%) during its crosslinking with HMDI at 60°C. (a) After 1 h in THF solution at 60°C. (b) Film at 60°C 1 h after casting. (c) Film at 60°C 3 h after casting. (d) Film at 60°C 6 h after casting.

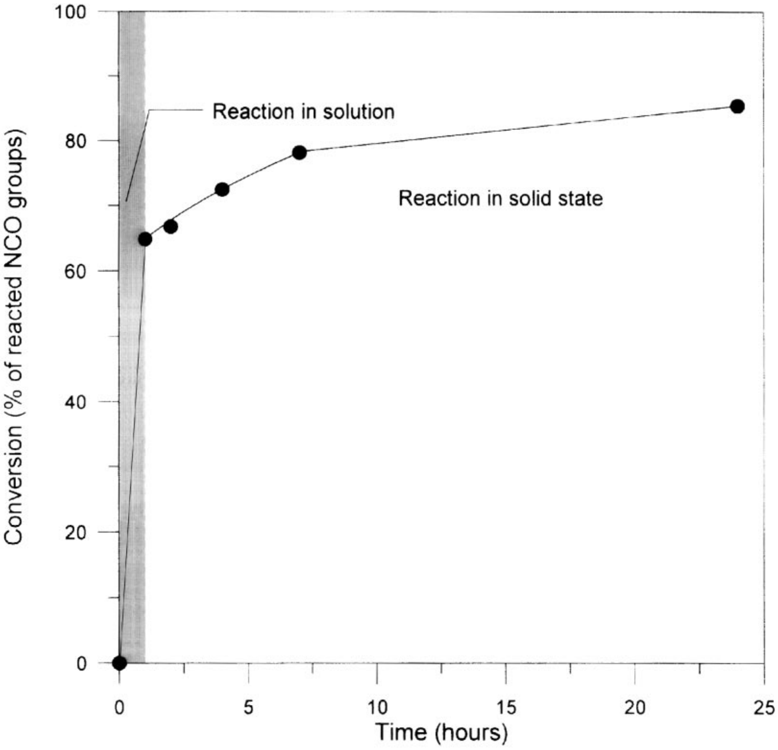


Fig. 9. Crosslinking kinetics, at 60°C, of hydroxylated PVC (13.2%) with an equimolar number of NCO groups.

followed by IR spectroscopy, progress rapidly and with high yield.

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