ELSEVIER

Polymer 43 (2002) 2631–2636

polymer

www.elsevier.com/locate/polymer

PVC modification with new functional groups. Influence of hydrogen bonds on reactivity, stiffness and specific volume

Miguel Herrero[a], Pilar Tiemblo[a], Juan Reyes-Labarta[b], Carmen Mijangos[a], Helmut Reinecke[a,*]

[a]*Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain*
[b]*Departamento de Ingeniería Química, Universidad de Alicante, Apdo. Correos 99, E-03080 Alicante, Spain*

Received 13 August 2001; received in revised form 29 November 2001; accepted 7 January 2002

Abstract

The chemical modification of PVC with new bifunctional thiol compounds is reported. Aliphatic as well as aromatic reactives were tested and the influence of protic and non-protic functionalities on reactivity was studied. The chemical structure of the polymers was analyzed using ^{1}H NMR spectroscopy.

The structural changes in the modified samples were monitored by means of density and T_g determinations, which are a measure of interchain spacing and chain stiffness. While protic functionalities lead to polymers with strongly enhanced T_g values indicating a considerable stiffening of the system due to physical interaction by hydrogen bonds, the softening-point temperature of PVC modified with non-protic substituents does not change very much.

The interchain spacing of the polymer is not significantly altered by the presence of mobile hydrogen in the polymer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Modified PVC; Glass transition temperature; Specific volume

1. Introduction

PVC is known as a highly versatile polymer with an excellent balance of properties and numerous applications, as water pipes, packaging and in the construction and medical sector. The use as a packaging material is due to its excellent film forming behavior and the fact that PVC is generally considered as a barrier polymer exhibiting relatively low permeation coefficients for certain gases that avoid or reduce the contact of air and humidity with the product, which is to be protected.

On the other hand, it has recently been shown [1,2] that PVC can also be used as an interesting starting membrane material for gas separation when the polymer is chemically modified. Using appropriate modification reactants, both permeability and selectivity of the membrane and different gas pairs could be significantly enhanced. A systematic study of the influence of modifier groups of different structure and size on the free volume and the flexibility of the system should, therefore, be of great interest.

Modification of PVC can generally be achieved by nucleophilic substitution reactions of chlorine atoms. Appropriate modification agents are characterized by a strong nucleophilic character while their basicity should be low in order to avoid dehydrochlorination [3–7]. If modification of the polymer is carried out to introduce functional groups [8] 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.

Bifunctional aromatic thiol compounds have been demonstrated to be appropriate reactants for the functionalization of PVC [9–11]. Under certain experimental conditions the modification reactions are extremely selective with respect to the mercapto group and the copolymers formed were 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 [12–14]. In this paper, the synthesis and characterization of PVC modified with a series of new aromatic and aliphatic thiol compounds is described and the influence of the type of functional group on reactivity is studied. In a second part, the influence of the functionality of a few selected polymers on interchain spacing and stiffness of the systems is investigated.

---

* Corresponding author. Tel.: +34-91-5622-900; fax: +34-91-5644-853.
E-mail address: hreinecke@ictp.csic.es (H. Reinecke).

0032-3861/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00064-2

2. Experimental part

Commercial bulk polymerized PVC with a weight average molecular weight of $M_W = 58\,000$ g/mol was obtained from ATOCHEM, Spain. The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8% and iso = 19.6%.

4-Mercaptophenol of technical quality (purity 90%) was purchased from Aldrich and was purified by distillation ($bp^{3\ Torr} = 120$ °C, Ref. [15]: $bp^{25\ Torr} = 149$ °C). ^{1}H NMR ($(CD_3)_2SO$): $\delta = 9.6$ (s, OH), $\delta = 7.3$ (d, 2ArH), $\delta = 6.8$ (d, 2ArH), $\delta = 4.9$ (s, SH).

4-Methoxybenzenethiol was purchased from Acros and used as received (purity 96%). The corresponding sodium salt was obtained by reaction with stoichiometric amounts of sodium hydride (60% dispersion in mineral oil (Aldrich)) in THF. After 24 h at room temperature the white salt was filtered, washed with hexane and dried. ^{1}H NMR ($(CD_3)_2SO$): $\delta = 7.3$ (d, 2ArH), $\delta = 6.8$ (d, 2ArH), $\delta = 3.8$ (s, OCH_3).

4-Mercaptobenzoic acid was purchased from Aldrich and used as received (purity 97%).

4-Mercaptobenzoic acid methyl ester was prepared according to a standard esterification method from 4-mercaptobenzoic acid in methanol with a catalytic amount of sulfuric acid. The ester was distilled under reduced pressure ($bp^{2\ Torr} = 105$ °C, Ref. [16]: $bp^{11\ Torr} = 139$ °C). Yield: 90% ^{1}H NMR ($(CD_3)_2SO$): $\delta = 7.3$ (d, 2ArH), $\delta = 6.8$ (d, 2ArH), $\delta = 4.9$ (s, SH), $\delta = 3.8$ (s, $COOCH_3$).

Mercaptoacetic acid was purchased from Aldrich and used as received (purity 97%).

Mercaptoacetic acid methyl ester was prepared according to a standard esterification method from 4-mercaptoacetic acid in methanol with a catalytic amount of sulfuric acid. The ester was distilled under reduced pressure ($bp^{16\ Torr} = 52$ °C, Ref. [17]: $bp^{15\ Torr} = 50$ °C). Yield: 72% ^{1}H NMR ($CDCl_3$): $\delta = 1.8$ (s, SH), $\delta = 3.3$ (s, 2H), $\delta = 3.65$ (s, 3H).

1-Mercapto-2-*N*,*N*-dimethylamino ethane was obtained in a two-step synthesis: 0.1 mol dimethylaminoethyl chloride was refluxed for 6 h in 50 ml of ethanol with 0.11 mol thiourea. After cooling the solution the corresponding uronium salts crystallizes. The filtered crystals were used without further purification and hydrolyzed under nitrogen atmosphere at 95 °C for 5 h with 60 ml of 5N aqueous sodium hydroxide solution. The reaction solution was cooled to room temperature and neutralized with 2N HCl solution to pH = 8. The mercapto compound was extracted with dichloromethane and purified by distillation ($bp^{10\ Torr} = 47$ °C). Overall yield: 50% ^{1}H NMR ($CDCl_3$): $\delta = 1.8$ (s, SH), $\delta = 2.25$ (s, 6H), $\delta = 2.5$ (t, 2H), $\delta = 2.6$ (t, 2H).

Cyclohexanone was bidistilled prior to use.

2.1. Modification of PVC

PVC (0.5 g, 8 mmol) and 8 mmol of mercapto compound with mobile hydrogen atoms (**R1b**, **R2b**, **R5b**) were dissolved in 50 ml of cyclohexanone. Potassium carbonate (1.6 g) was added and the reaction started under N_2-atmosphere at 60 °C (route I). Modification with mercapto compounds which do not exhibit mobile hydrogen (**R1a**, **R2a**, **R5a** and **R6a**) was performed without potassium carbonate using the corresponding sodium salts of the compounds (route II) obtained by reaction with sodium hydride according to a procedure described elsewhere [10].

The reactions were stopped by precipitating the mixture in cold methanol/water (2:1). The modified polymers were purified using THF/methanol (for samples with a degree of modification of less than 20%) or THF/hexane (for higher modified samples) as a solvent–precipitant system.

Degrees of substitution of the modified polymers, expressed as mol% of ethyl thiol compound units/(ethyl thiol compound units + chloroethane units), was determined by ^{1}H NMR. Spectra were recorded at 25 °C on a 200 MHz XL Varian spectrometer operating at 200 MHz using 5% solutions in deuterated dimethyl sulfoxide or in mixtures of deuterated chloroform and deuterated nitrobenzene.

IR measurements were performed on thin solvent cast films of the modified polymers using a Nicolet 520 FTIR spectrometer.

The calorimetric measurements of the modified PVC samples were carried out using a Perkin–Elmer differential scanning calorimeter DSC-7. Samples of about 10 mg were heated up to 150 °C under a nitrogen atmosphere at 20 °C/min and quenched at a cooling rate of 200 °C/min. The T_g values reported were taken from the second runs (heating rate 15 °C/min) and correspond to the midpoint of the DSC curves measured from the extension of the pre- and post-transition baseline.

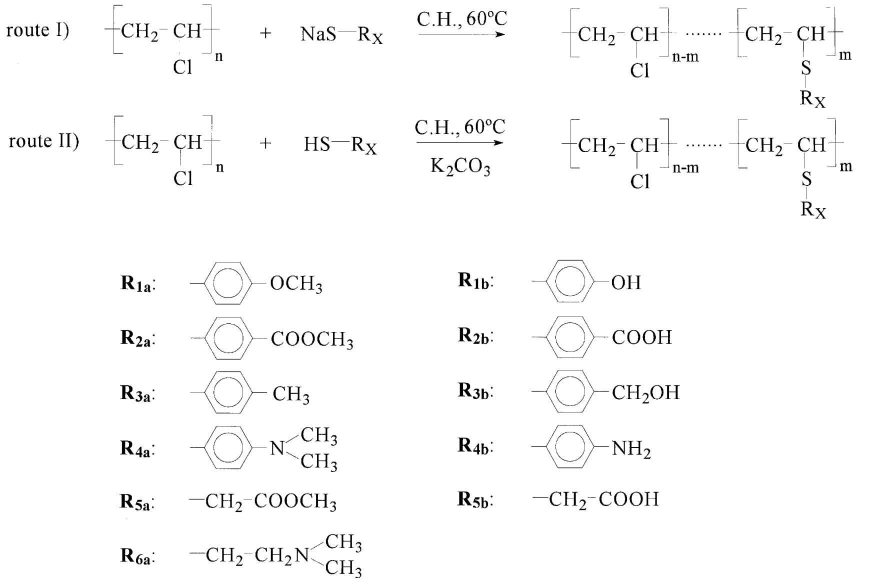
2.2. Density measurements

The densities of the films were determined by the flotation method at 20 °C using water and an aqueous solution saturated with $ZnCl_2$. The composition of the solution was adjusted in such a way that the films just remained suspended throughout. Care has been taken to eliminate all bubbles sticking to the films using an ultrasonic bath. To minimize the error, four different sample pieces for each polymer were used. The densities of the mixtures were determined using a pygnometer. The relative experimental error is less than 0.001 g/cm^3.

3. Results and discussion

3.1. Chemical constitution of the modified PVC

The reactivity of new mercapto compounds containing a second functional group is tested with respect to chlorine substitution in PVC. The reactants used can be divided into two groups. The first one (series **RXb**) exhibits, apart from



Scheme 1. Nucleophilic substitution of PVC with chemical constitution of the modified polymers.

the mercapto moiety, a functionality with mobile hydrogen atoms, which allow the formation of hydrogen bonds in the modified polymer while in the second group (series **RXa**) these hydrogen atoms are substituted by methyl groups which prevent this kind of interaction.

In Scheme 1 the nucleophilic substitution reaction on PVC with the thiol compounds studied in this work is depicted. The experimental conditions used and results of the modification reaction are summarized in Table 1. From these data several conclusions can be drawn.

It is confirmed that the use of aliphatic thiols leads to degrees of modification which are much lower than those achieved with aromatic ones. Furthermore, nucleophilic substitution of chlorine atoms by aliphatic thiols is always accompanied by a considerable amount of dehydrochlorination as an undesired side product.

On the other hand, when using aromatic thiols no elimination is observed as a side reaction but in some cases crosslinked polymers may be obtained. In the case of thiol compounds where the second functional group also exhibits acid–base activity, the capability of this group to act as a nucleophile is the factor which determines if it remains intact or if a second substitution reaction on the polymer chain can take place leading to crosslinked systems. Aromatic primary amines (**R4b**) have been shown to be not basic enough to react under the chosen conditions what allowed the formation of PVC with free amino groups [11]. In all other reactants of the series **RXb** shown in Table 1 the second functional group is less basic or even acid. In this latter case also the acidity of this group and the basicity of the corresponding base-pair has to be considered to understand the reactivity of these compounds in a nucleophilic substitution reaction. It can be supposed that very strongly acid groups dissociate completely in the basic

Table 1
Reaction conditions and results of the substitution reactions on PVC

Polymer	Functional group	Route	Reaction time (h)	Maximum degree of modification (%)	Observations
R1a	*p*-Arom-OCH_3	II	24	68	No side reaction
R1b	*p*-Arom-OH	I	24	33	No side reaction
R2a	*p*-Arom-$COOCH_3$	II	24	68	No side reaction
R2b	*p*-Arom-COOH	I	6	–	Crosslinked
R3a	*p*-Arom-CH_3	II	24	65	No side reaction
R3b	*p*-Arom-CH_2OH	I	24	32	No side reaction
R4a	*p*-Arom-$N(CH_3)_2$	II	24	67	No side reaction
R4b	*p*-Arom-NH_2	I	24	33	No side reaction
R5a	Aliph-$COOCH_3$	I	24	8.6	Elimination: 1.3%
		II	24	5.1	Elimination: 1.7%
R5b	Aliph-COOH	I	5	–	Elimination, crosslinked
R6a	Aliph-$N(CH_3)_2$	I	24	9.7	Elimination: 11.9%

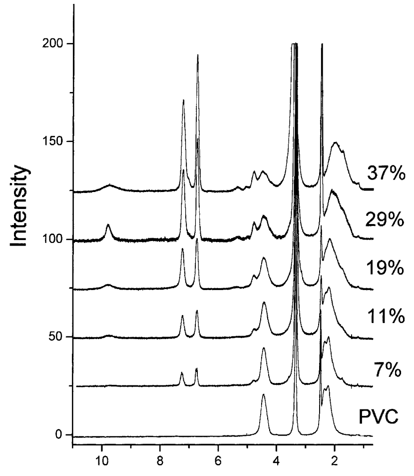


Fig. 1. Evolution of the ^{1}H NMR spectra upon conversion for the modification of PVC with 4-mercaptophenol.

reaction medium used. The base-pair of a strong acid, however, is a very weak nucleophile and no nucleophilic attack should take place. On the other hand, in the case of very weak acids like aliphatic alcohols, the corresponding base (alcoholate anion) would have a strongly basic character and would cause serious degradation of the PVC by dehydrochlorination. As has been shown earlier [8], 4-mercapto benzylalcohol can be used to obtain polymer **R3b** without side products indicating that the alcoholate is not formed in the moderately basic medium of cyclohexanone/potassium carbonate.

Functional groups as the carbonyl group with an acidity between these two extreme cases are not appropriate for our purpose as can be seen in the examples **R2b** and **R5b**. The compounds used for modification (4-mercaptobenzoic acid and mercapto acetic acid) are acid enough to allow the formation of a certain quantity of carboxylate anions which, on there turn, are sufficiently basic to cause substitution of chlorine atoms leading to crosslinked products.

An interesting case is the use of 4-mercaptophenol. The phenol group is about two orders of magnitude less acid than a carboxylic acid. If its acidity is so weak that the corresponding base cannot be formed under the experimental conditions used, it should be possible to obtain PVC with free phenolic groups. On the other hand, if only small amounts of phenolate anions are built in the solution these would react as strongly basic nucleophiles and crosslinked products with a considerable amount of dehydrochlorination in the polymer main chains could be expected.

In Fig. 1 ^{1}H NMR spectra of PVC modified with 4-mercaptophenol to different degrees of modification are shown. With increasing reaction time, aromatic (7.3 and 6.8 ppm) as well as phenolic proton peaks (9.8 ppm) arise in the modified polymers. The signal of the CH–Cl protons at 4.5 ppm decreases with conversion, while a new one at 4.8 ppm is formed due to CH–S protons. For conversions higher than 20% further peaks at 5.05 and 5.35 ppm are observed which are due to the effect of the chemical composition distribution [10,12] which becomes broader when the number of modifier groups in the polymer increases.

The degree of modification $U(\%)$ can be easily calculated from the NMR spectra using the formula: $U(\%) = I(6.8\ \text{ppm}) \times 50/[I(\text{CHCl}) + I(\text{CHS})]$, where I are the integrals of the respective proton signals.

The NMR analysis reveals some important features of this modification reaction: 4-mercaptophenol is a suitable agent to form PVC with free hydroxy groups, as indicated by the NMR peak at 9.9 ppm; the nucleophilic substitution reaction is completely selective with respect to the mercapto group what is indicated by the fact that the ratio of aromatic to hydroxy proton peaks is 4:1, independent of conversion; this modification reaction is free of undesired side reactions like elimination or crosslinking as can be deduced from the absence of corresponding olefinic protons at about 5.8 ppm. Thus, white THF-soluble products are obtained.

In Fig. 2, the conversion of the modification reaction of PVC with 4-mercaptophenol (**R1b**) is shown as a function of time and compared with that of PVC modified with 4-methoxybenzenethiol (**R1a**). Both reactions reach an equilibrium state after about 15 h. A significant difference can be stated with respect to the maximum conversions obtained. While in polymer **R1b** only about 35% of the present chlorine atoms are substituted under the given conditions, in system **R1a** the maximum degree of substitution is nearly twice as high. In Table 1 it can be seen that this trend is generally observed when comparing modifications using reactants of the series **RXb** with those of series **RXa**. The difference in reactivity and final degree of modification between these two classes of reactants can easily be explained by the formation of hydrogen bonds between polymer chains in the first case. This kind of interactions leads to a physical crosslinking of the system and limit thereby the access of modifier molecules to the reactive sites of the polymer.

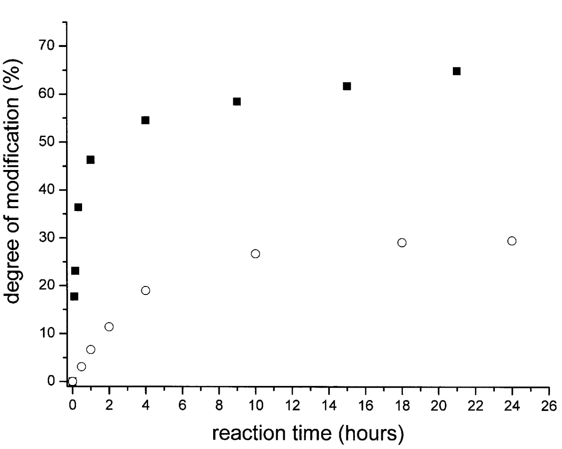


Fig. 2. Conversion of the modification reactions as a function of time for PVC modified with 4-mercaptophenol (○) and methoxybenzenethiol (■).

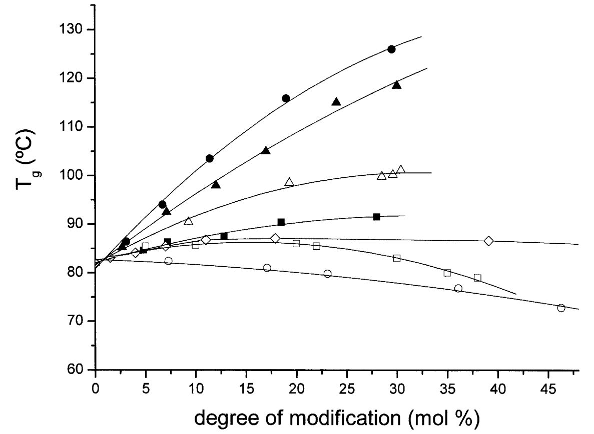


Fig. 3. Evolution of T_g with modification degree of **R1a** (○), **R1b** (●), **R2a** (◇), **R3a** (□), **R3b** (■), **R4a** (△), **R4b** (▲).

3.2. Influence on T_g

Chain stiffness is one of the main structural parameters to be taken into account when considering a given polymer for applications in gas transport processes. A property related to the chain stiffness is for example the glass transition temperature T_g. The study of the calorimetric properties of the modified PVCs was performed by DSC measurements. In all investigated polymers only one glass transition temperature is detected, indicating the absence of block copolymer structures. The T_g values obtained from the DSC curves were plotted against the molar conversion in Fig. 3. It can be seen that the evolution depends strongly on the modifier group introduced in the PVC chains. While a strong increase of T_g of up to 40 °C is observed in PVC modified to 30% with phenol or aniline groups, substitution of chlorine by thiocresol (**R3a**) or methoxy benzenethiol (**R1a**) does not produce dramatic changes in the softening point temperature which remains more or less constant over a large range and then slightly decreases for high values of modification degrees.

In general, the T_g of a polymeric material depends on the chain segment mobility. If modification is carried out in the side chain of the system the molecular motions of the main chains are influenced by the size of the substituents and/or by the introduction of functional groups, which cause physical interaction between chains.

In the present case, all substituents used are *para*-substituted aromatic mercapto compounds having a size of the same order of magnitude. The strong increase of T_g in polymers **R1b** and **R4b** observed is consequently due to physical interactions between chains produced by hydrogen bonds. In the phenol group the proton is relatively acid and well available for this kind of interactions. Also in PVC modified with mercapto benzylalcohol (**R3b**) an increase of T_g with increasing modification degree can be stated, but the protons of an aliphatic alcohol are several orders of magnitude less acid than that of a phenol. Therefore, their possibility to form hydrogen bonds is limited and consequently the increase of T_g in this case is less pronounced.

The steric influence of the modifier group on chain stiffness can be studied in the polymers modified with methoxybenzene (**R1a**) and *N*,*N*-dimethylaniline (**R4a**) moieties. These polymers differ mainly in one methyl group in the side chain. This small structural difference, however, leads to a difference in T_g of 20 °C for a degree of substitution of 30% showing the sensitivity of the steric influence on chain mobility.

3.3. Influence of free volume

The second parameter which strongly influences the gas transport properties of a polymeric membrane is its free volume. As has been seen above, the introduction of protic functional groups in PVC favors physical interactions between chains by the formation of hydrogen bonds and leads to an increase of stiffness of the system. In order to see how the use of different modifier groups is reflected in the free volume, films were prepared from THF solution and their density determined by flotation method. As it is known, that some properties of these samples vary with time due to physical aging phenomena, measurements were performed four weeks after preparation of the films, period which has been shown to be necessary until a pseudoequilibrium state is reached [1].

The evolution of density with the modification degree of four selected modified PVC systems is depicted in Fig. 4. In all four systems, the introduction of any of the substituents brings about a considerable decrease of density; a decrease, which at low conversions is in magnitude very similar in the four systems. That density decreases on introducing any of these bulky groups is an expected result, as the density of the 100% substituted polymers, as calculated by group contribution [18], is lower than that of PVC. However, in

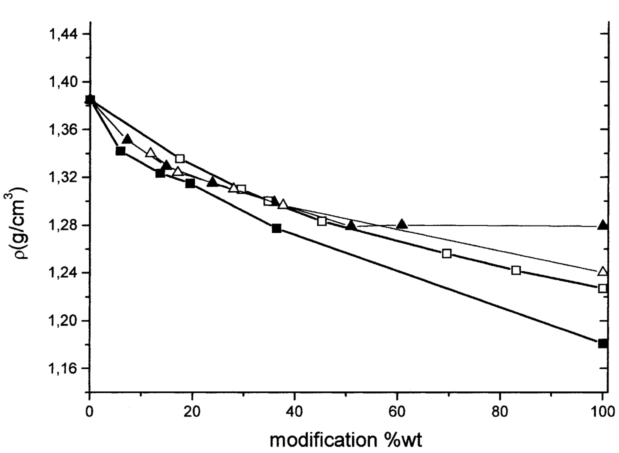


Fig. 4. Evolution of density with modification degree for **R1a** (□), **R1b** (▲), **R3a** (■), **R3b** (△). The density of the 100% substituted polymers have been calculated by group contribution [15].

all four cases, the density decrease is stronger as expected, and thus, a negative deviation with respect to the additive straight line is observed.

The decrease in density upon modification is easily explained by the bulkiness of the substituents which hinders chain packing of the modified PVC. In a first stage, at low degrees of substitution, the introduction of each modifier group contributes very efficiently to this hindering of the chain packing, while at higher degrees of modification new substituents enter sites where the chains are already separated. Consequently, the slope of the curves diminishes with increasing modification, more so the higher the density of the modified units.

The fact that no strong influence in chain packing and free volume is produced by protic functional groups which have been shown to dramatically increase the chain stiffness, might be surprising. However, it is likely that low concentrations of hydrogen bonds which are strong enough to stiffen the system do not have the sufficient strength to efficiently hold chains tight together and produce an increase of the density.

4. Conclusions

PVC can be chemically modified introducing a wide range of different functional groups. When aromatic mercapto compound are used and appropriate reaction conditions are chosen, only nucleophilic substitution of chorine takes place while dehydrochlorination is completely suppressed. Reactants with non-protic functional groups can be introduced in the chains up to degrees of modification of 65%. In the case where the mercapto compound carries protic functionalities the reactivity of the reactive depends on its acidity and in no case substitution degrees of higher than 35% are reached.

The introduction of bulky groups in the chains of PVC leads to chain separation and results in a large increase of free volume which depends little on whether protic or non-protic functional groups are introduced. The possible formation of hydrogen bonds in the former case, however, leads to a significant increase in chain stiffness.

The gas transport properties of these modified polymeric systems will be the subject of a further publication.

Acknowledgements

We acknowledge financial support from the Consejería de Cultura de la Comunidad de Madrid (BIO-009-2000), CICYT MAT1999-1127-C04-01 and MAT 99-1179.

References

[1] Tiemblo P, Guzmán J, Riande E, Mijangos C, Reinecke H. Polymer 2001;42:4817.
[2] Tiemblo P, Guzmán J, Riande E, Mijangos C, Reinecke H. Macromolecules 2002;35(2):420.
[3] Cassagnau P, Bert M, Michel A. J Vinyl Technol 1991;13(2):114.
[4] Anzai JJ, Liu CC. Polym Commun 1992;31:346.
[5] Pourahmady N, Bak P. J Macromol Sci 1992;A(29):959.
[6] Bromberg L, Levin G. J Appl Polym Sci 1993;49:1529.
[7] Hears MS, Baird JD, Nethsinghe LP, Gilbert M. Polym Commun 1990;31:194.
[8] Reinecke H, Mijangos C. Makromol Chem Rapid Commun 1996;17:15.
[9] Reinecke H, Mijangos C. Polym Bull 1996;36:13.
[10] Reinecke H, Mijangos C. Macromol Chem Phys 1998;199:2199.
[11] Reinecke H, López D, Mijangos C. J Appl Polym Sci 1999;74:1178.
[12] Mijangos C, López D. Macromolecules 1995;28:1369.
[13] Millán J, Martínez G, Mijangos C. J Polym Sci, Chem Ed 1985;23:1077.
[14] Mijangos C, Gómez-Elvira JM, Martínez G, Millán J. J Appl Polym Sci 1989;38:1685.
[15] Burawoy L. Tetrahedron 1958;4:403.
[16] Wiley J. J Org Chem 1951;16:810.
[17] Baker A. J Org Chem 1947;12:144.
[18] Van Krevelen DW. Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contribution. 3rd ed. Amsterdam: Elsevier, 1990. p. 71–80.