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Modification of poly(vinyl chloride) with new aromatic thiol compounds. Synthesis and characterization

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Abstract

Different thiol compounds were tested for the synthesis of poly(vinyl chloride) (PVC) with halogen groups and the course of the modification reactions followed under different conditions by NMR spectroscopy and elemental analysis. It is shown that PVC can be modified without side reactions using 4-fluorothiophenol, 4-chlorothiophenol, 4-bromothiophenol, 3,4-di-fluorothiophenol, penta-fluorothiophenol and penta-chlorothiophenol. The reactivities and final degrees of modification of the different nucleophiles are compared showing that, when the thiolate salt is preformed, the bromine derivative reacts quicker and higher degrees of modification are reached than with its smaller homologues. On the other hand, using the thiol compounds in combination with potassium carbonate this order is inverted and highest degrees of modification are achieved with 4-fluorothiophenol. Glass transition temperatures and thermal stabilities of the new compounds are compared.
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1. Introduction

Poly(vinyl chloride) (PVC) is known as a highly versatile polymer with an excellent balance of properties and numerous applications in the construction and medical sector, as water pipes or for packaging purposes. The application of polymer analogous reactions on PVC has been shown to open even more fields for useful applications of this polymer [1,2].

Modification of PVC can generally be achieved by nucleophilic substitution reactions of chlorine atoms [3−16]. Appropriate modification agents are characterized by a strong nucleophilic character while their basicity should be low in order to avoid dehydrochlorination. It is well established now that the most efficient nucleophiles for PVC modification are aromatic thiol compounds [17−20]. These reagents can be incorporated into the polymer with high conversions and

without secondary reactions when appropriate reaction conditions are employed. Furthermore, it was shown that this type of reaction is stereoselective and can be performed in solution, melt, suspension [21−23] or selectively at the surface of a polymer film [24,25].

In the present paper the synthesis and characterization of PVC modified with a series of new aromatic thiol compounds carrying different halogen moieties are described and the influence of the aromatic substituents on the reactivity is studied. There are two main reasons for choosing these agents. On the one hand, the commercial availability of a homologous series of monosubstituted *p*-halogenthiophenols makes these compounds as suitable materials for the preparation of model compounds interesting for the study of different aspects of basic research. On the other hand, fluorine containing polymeric compounds are of practical interest due to their thermal and chemical resistance and very low adhesion properties. The interest for the study of PVC modified with penta-chlorothiophenol lies in the fact that low molecular penta-chlorophenol is an extremely efficient pesticide and fungicide that is used

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as an additive for soft PVC in applications as bathroom curtains etc. Additives of low molecular weight, however, are known to migrate out of the polymer, which finally can lead to the loss of the related properties. The covalent linkage of this additive to the polymer chain might be a solution for this inconvenience.

In the present paper we describe the synthesis, characterization and reaction kinetics of PVC with the before mentioned thiol compounds.

2. Experimental

2.1. Materials

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were $M_w = 112{,}000$ g/mol and $M_n = 48{,}000$ g/mol. The tacticity measured by ^{13}C NMR was syndio = 30.6%, hetero = 49.8% and iso = 19.6%.

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

p-Fluorothiophenol (F-TP), *p*-chlorothiophenol (Cl-TP), *p*-bromothiophenol (Br-TP), penta-chlorothiophenol (Cl5-TP), 3,4-di-fluorothiophenol (F2-TP) and penta-fluorothiophenol (F5-TP) were purchased from Aldrich. The corresponding sodium salts were obtained by reaction with stoichiometric amounts of sodium hydride (60% dispersion in mineral oil (Aldrich)) in THF. After 2 h at room temperature the solutions were filtered and the white salts precipitated and washed with hexane.

2.2. Modification of PVC with mercapto compounds

PVC of 8 mmol (based on monomer units ($M = 62.5$ g/mol)) and 8 mmol of the respective aromatic thiol compound were dissolved in 50 ml of cyclohexanone, 1.6 g of potassium carbonate was added (only in the cases where the mercapto compound is used instead of its sodium salts) and the reaction started under N_2-atmosphere at 60 °C (for cyclohexanone). The reaction was stopped by precipitating the mixture in cold methanol/water (2:1). The modified polymers were purified using THF/methanol or THF/hexane as a solvent−precipitant system.

2.3. 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 ^1H NMR. Spectra were recorded in 5−10% (w/w) solutions with a Varian Gemini 300 (300 MHz, $T = 25$ °C, 16 scans, pulse width 20 μs). The solvents were purchased from Scharlau (DMSO-d_6), sds (CDCl$_3$) and Aldrich (pyridine-d_5) and had levels of deuteration of 99.8% (DMSO, CDCl$_3$) and 99.0% (pyridine), respectively.

Elemental analysis of the penta-halogenated samples was performed on a CHNS-932 of Leco.

IR spectra were recorded at ambient temperature on a Spectrum One FTIR spectrometer of Perkin−Elmer equipped with a diamond internal reflection element, using an accumulation of 4 runs and the same pressure of the crystal on the surface in each sample.

Glass transition temperatures of the samples were determined using a DSC7 calorimeter of Perkin−Elmer. The heating rate was 10 °C/min.

Thermal stabilities were measured on a TGA Q500 of TA Instruments by heating the samples from 50 to 600 °C under N_2 with a heating rate of 10 °C/min.

Dynamic mechanical relaxation was measured with Polymer Laboratories MK II DMTA working in tensile mode at constant stress. The complex modulus, $E = E' + E''$, of each sample was determined at frequencies of 1, 3, 10, and 30 Hz over a temperature range from 193 K to about 393 K. Samples were prepared from extracted films, obtained as described above. The experiments were carried out at a heating rate of 1.5 K/min. The dimension of the specimens was around 150−200 μm in thickness, 2 mm in width, and 1.0−1.5 cm in length.

The apparent activation energies of the relaxation processes were calculated according to an Arrhenius-type equation from the maximum values of the loss modulus at the four mentioned frequencies. The accuracy achieved in the temperature assignment of the loss maximum was estimated to be about ±1 K.

3. Results and discussion

Modification of PVC was carried out using two series of commercial halogen-containing thiol compounds, mono- and penta-substituted ones, and furthermore a di-fluorinated aromatic thiol modifier. The modification reaction of different compounds with PVC is depicted in Scheme 1. The reaction conditions are described in Section 2.
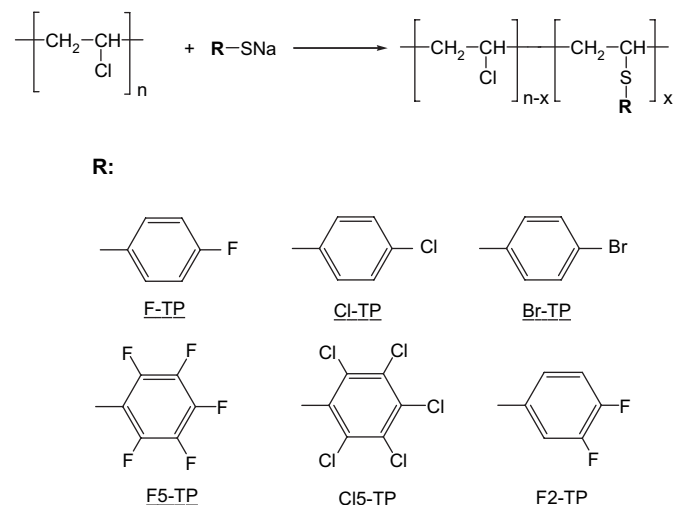
Scheme 1. Modification reaction of PVC with different halogenated thiol compounds.

3.1. Mono-halogenated thiophenol modifier

The chemical structure of the products obtained in the case of the mono-halogenated thiophenol modifiers was analyzed using ^{1}H NMR spectroscopy. As an example, in Fig. 1 the evolution of the ^{1}H NMR spectra upon conversion of PVC modified with 4-fluorothiophenol is shown. With increasing reaction time, aromatic peaks (7.5 and 7.3 ppm) arise in the modified polymers. The signal of the CH–Cl protons at 4.5 ppm decreases with conversion and broadens considerably, while new bands arise around 4.8 and 3.3 ppm (the latter superposed by the water peak of the solvent). The latter ones are due to CH–S protons while variety of new signals between 4 and 5 ppm have been shown to be caused by the effect of the chemical composition distribution [21] which becomes broader when the number of modifier groups in the polymer increases. The changing intensities of the aromatic proton peaks at 7.3 and 7.5 ppm with the degree of modification have also been observed in similarly modified PVC systems [19] and had been demonstrated to be due to the stereoselective character of the modification reaction.

The degree of modification U (%) can be easily calculated from the NMR spectra using the formula: U (%) = I (8–7 ppm)/[$4*I$ (5–4 ppm) + $I(I$ (8–7 ppm))], where I is the integrals of the respective proton signals.

The NMR analysis reveals some important features of this modification reaction: 4-fluorothiophenol and its homologues are suitable agents that allow the incorporation of a large number of aromatic halogen groups into the polymer. Under the chosen experimental conditions the modifiers react very selectively with respect to nucleophilic substitution while side reactions due to dehydrochlorination are strongly suppressed.

In Fig. 2, the conversions of the modification reactions of PVC with 4-fluorothiophenol, 4-chlorothiophenol and 4-bromothiophenol are shown as a function of time. The reaction kinetics have been recorded under two different experimental
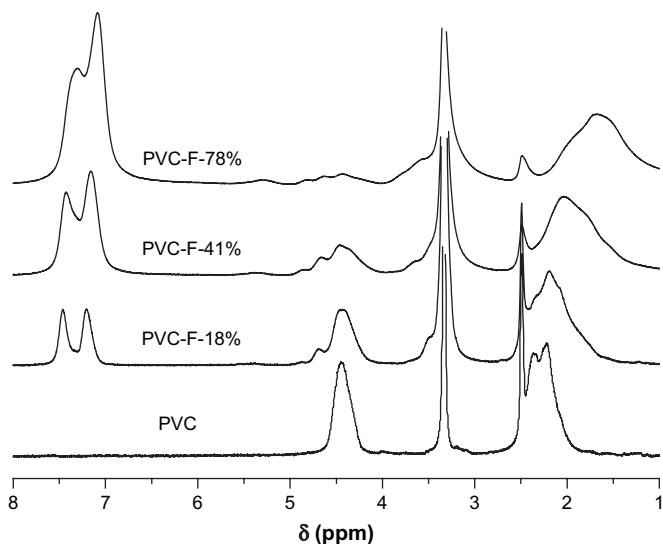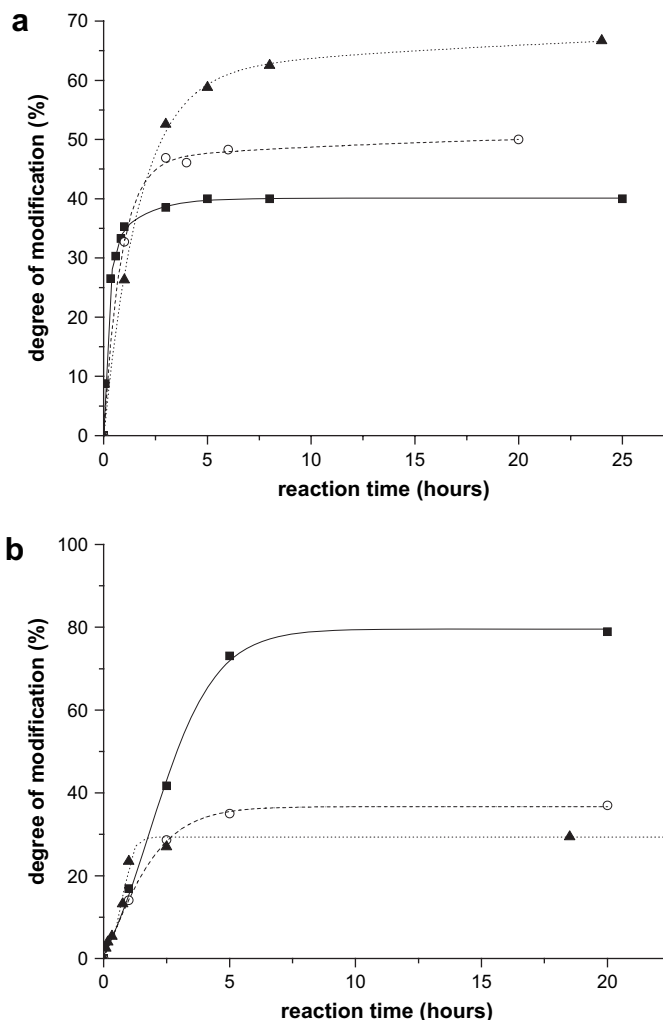
Fig. 2. Conversions of the modification reactions of PVC with 4-fluorothiophenol (■), 4-chlorothiophenol (○) and 4-bromothiophenol (▲) as a function of time using (a) the thiolate salts and (b) forming the salt in situ with a combination of the thiol and potassium carbonate.

conditions: in the first case the thiolate salts were formed and isolated in a previous step to the modification reaction, in the second case the 4-halogenthiophenol was used in combination with an excess of potassium carbonate as a weak base which forms the corresponding thiolate salt in situ.

Fig. 2a shows the resulting reaction kinetics for the first case and Fig. 2b for the second case. First of all one can see that in all cases highly modified polymers can be obtained after relatively short reaction times and that the three modifiers show different behaviours with respect to their kinetic and thermodynamic equilibrium that is reached. When the thiolate salt is preformed in a previous step the highest degree of modification is obtained with 4-bromothiophenol (68%) and the lowest one with 4-fluorothiophenol (40%). This tendency corresponds to the acidity and nucleophilicity of the modifier which, on the other hand, are influenced by the inductive (I) and mesomeric (M) effects of the substituents. As fluorine has the strongest −I effect of the three substituents tested here, the corresponding thiol has a higher acidity and the salt formed will be more

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

stable and consequently less nucleophile than 4-bromothiophenol. However, observing the curves at short reactions times it becomes evident that the fastest reaction is that with the fluorine modifier and the slowest one that with bromine. This kinetic effect might be due to the size of the modifiers as fluorine is considerably smaller than bromine which favours on the one hand the mobility of the nucleophile and, on the other hand, the access to the reactive sites of the polymer.

Interestingly, things are inversed when the modification reactions are carried out using instead of the preformed thiolates the thiols in combination with a base forming the reactive salt in situ. In this case (Fig. 2b) the highest degrees of modification are reached with 4-fluorothiophenol and the lowest with 4-bromothiophenol. The reason might be again the higher acidity of the former due to the stronger −I effect mentioned above which leads to a quicker and more complete salt formation. As a consequence of the higher salt concentration of the fluorine derivative in the medium, the thermodynamic equilibrium is more strongly shifted to the side of the products of the substitution reaction. While this argument can explain a possible inversion of the reactivities it remains still unexplained why using the preformed 4-fluorothiophenolate the degrees of modification that can be reached under the experimental conditions is considerable less (40 versus 80%) when the same salt is formed in situ.

3.2. Penta-halogenated thiophenol modifier

The second class of halogenated thiols tested here as reactants for the nucleophilic substitution of chlorine in PVC contains five halogen atoms in the aromatic ring. The first point of interest with these modifiers is again whether substitution or elimination takes place and to what extent. One problem of the prepared modified polymers is their characterization by ^{1}H NMR spectroscopy. While the mono-halogenated modifiers contain aromatic protons that allow an easy determination of the degree of modification of these systems using ^{1}H NMR in the polymers modified with penta-halogenated aromatic thiols, protons do only exist in the main chains of the polymer. These protons can be used to study double bond formation due to possible elimination side reactions but do not give information about the total degree of modification. One has, therefore, to find an alternative analytical method. We have chosen IR spectroscopy in order to obtain relative degrees of modification. Elemental analysis was used to record a calibration curve and calculate absolute values for the degree of modification.

In Fig. 3 the evolution of a PVC IR spectrum upon modification with penta-fluorothiophenolate sodium salt is shown. One can see that two new signals at 1465 and 956 cm^{-1} arise which correspond to the aromatic C=C bonds and the C−F bonds, respectively. These signals do also appear in the IR spectrum of the pure modifier. The IR spectra show also the complete absence of bands between 1600 and 1700 cm^{-1} which would correspond to olefinic double bonds. The absence of olefinic protons in ^{1}H NMR (not shown here) confirms the selectivity of the penta-halogenated modifiers with respect to nucleophilic substitution. At first sight this result
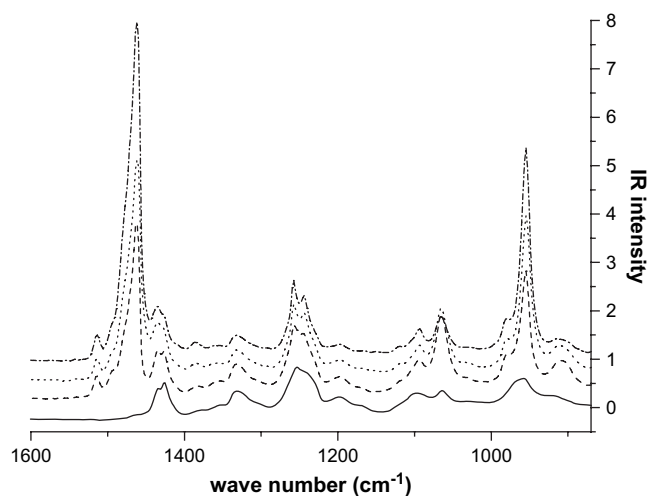

Fig. 3. Evolution of IR spectrum of PVC (solid line) upon modification with penta-fluorothiophenolate sodium after 1 h (dashed line), 4 h (dotted line) and 19 h (dashed-dotted line).

might be surprising because the electron density of the sulphur atoms of the thiol compounds and consequently their nucleophilicity can be supposed to be considerably reduced by the five aromatic substituents with a strong −I effect. From the absence of elimination by-products one has, therefore, to conclude that this negative inductive effect is overcompensated by the positive mesomeric effect characteristic for halogen moieties.

Elemental analysis was used to determine the molar percentage of sulphur atoms in the modified polymers and to calculate their degree of modification. In order to facilitate the analysis of the products these degrees of modification were then related to IR spectroscopy. The IR spectra were first normalized with respect to the signal of the C−H bonds of the PVC chains at 1430 cm^{-1}. The obtained values from elemental analysis were then used to calibrate the intensity of the IR signal at 1465 cm^{-1} (Fig. 4). With this procedure the conversion of the modification reaction of PVC with
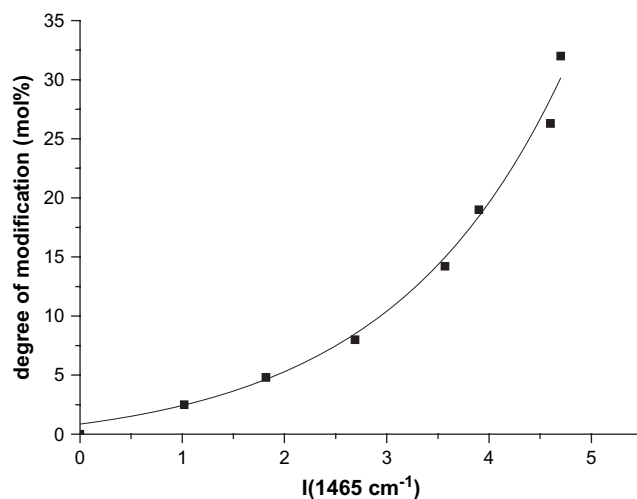

Fig. 4. Calibration curve relating IR band intensities at 1465 cm^{-1} with the degree of modification determined by elemental analysis.

penta-fluorothiophenol could be determined as a function of time. As in the case of the mono-halogenated thiol compounds the reaction kinetics were recorded under two different experimental conditions: (i) using the preformed sodium thiolate salt and (ii) forming the salt in situ using the thiol in combination with potassium carbonate. In Fig. 5a and b the conversions of the modification reactions of PVC with penta-chlorothiophenol and penta-fluorothiophenol as a function of time are compared. In both cases, (i) and (ii), approximately identical final conversions at equilibrium are obtained using the thiolate salt or the combination of thiol and potassium carbonate and the reactions have been finished after about 24 h. However, the penta-fluorothiophenol modifier appears to be a much stronger nucleophile than its homologue, being the final degree of substitution that is achieved around 33% (the maximum value possible in this case is 50% as the molar ratio PVC/thiol used was 2:1) while in the case of

penta-chlorothiophenol only 23% was reached (the molar ration PVC/thiol here being 1:1). This result confirms that the negative inductive effect of the halogen substituents is overcompensated by their positive mesomeric effect which is known to be stronger in the case of fluorine as here the overlap of p orbitals between 2p orbitals in fluorine and 2p orbital in carbon is more efficient (due to their comparable size) than the overlap of 3p orbitals in chlorine and 2p orbitals in carbon.

3.3. Thermogravimetric studies of the modified PVC

The thermal stability of the modified polymers was studied by TGA. The results of these measurements are summarized in Table 1. From these data it is concluded that no significant change of the stability with respect to PVC takes place upon modification when the thiol modifier contain chlorine or bromine atoms. However, thiol compounds containing fluorine are relatively efficient and lead to polymers whose onset degradation temperature is shifted to significantly higher values. In Fig. 6, the TGA thermograms of pure PVC (full line) and PVC modified with the two different fluorinated thiol compounds studied at several degree of modification are compared. In all cases, a first small weight loss is observed at low temperatures, which is associated to the loss of absorbed moisture and/or with the evaporation of trapped solvent. The next weight loss process corresponds to the degradation of the chain sequences containing the most labile chlorine atoms. At this point, it is observed that in the modified polymers these
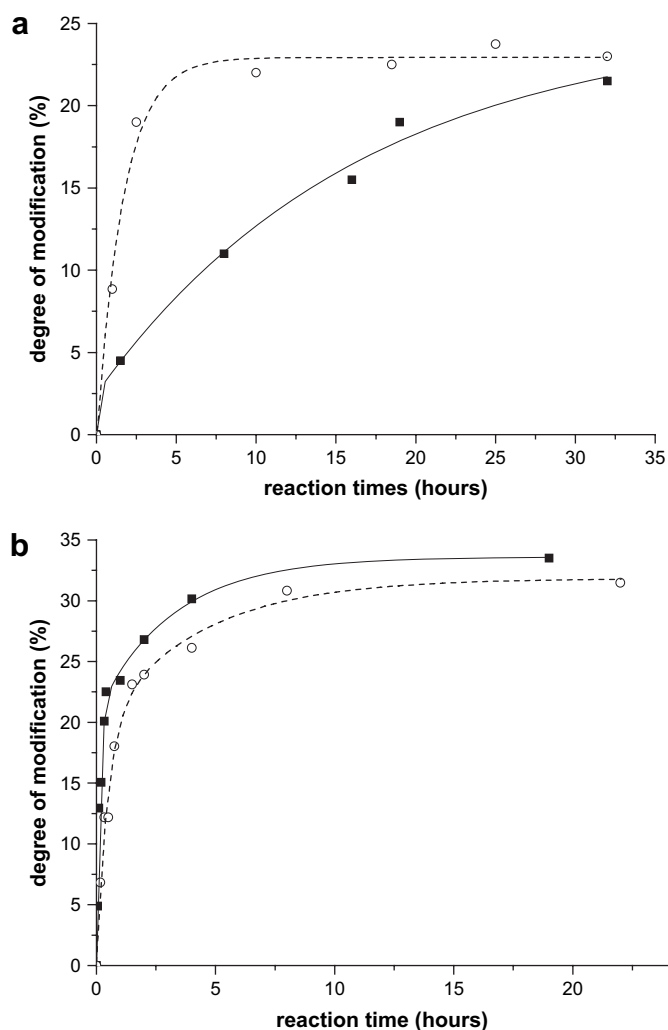

Fig. 5. (a) Kinetics of PVC modification in cyclohexanone at 60 °C with (i) penta-chlorothiophenol/K_2CO_3 (■) and (ii) penta-chlorothiophenolate sodium salt (○) using a 1:1 molar ratio of PVC and thiol compound. (b) Kinetics of PVC modification in CH at 60 °C with (i) penta-fluorothiophenol and K_2CO_3 (■) and (ii) penta-fluorothiophenolate sodium salt (○) using a 2:1 molar ratio of PVC and thiol compound.

Table 1
Thermal properties of modified PVCs

| Sample	$T_{D-onset}$ (°C)	Weight loss 1 (%)	Residue at 600 °C (%)	T_g (°C)
Pure PVC	275	61.3	7.9	83
PVC-Br-TP-10%	274	63.1	8.4	84.1
PVC-Br-TP-18.4%	268	63.0	7.0	83.6
PVC-Br-TP-26.3%	261	63.3	6.1	80.6
PVC-Br-TP-37.2%	262	63.1	6.1	81.4
PVC-Br-TP-46.8%	258	63.1	7.2	82.9
PVC-Br-TP-52.6%	258	63.0	4.4	80.1
PVC-Br-TP-66.7%	256	63.3	3.7	78.8
PVC-Cl-TP-7.7%	273	63.1	10.4	83.6
PVC-Cl-TP-16.4%	271	61.5	6.8	84.4
PVC-Cl-TP-23.3%	272	63.1	7.3	82.6
PVC-Cl-TP-32.7%	263	63.0	5.9	83.9
PVC-Cl-TP-47.8%	264	63.3	4.8	81.4
PVC-Cl5-TP-8.5%	275	63.1	8.8	80.8
PVC-Cl5-TP-17.9%	272	61.5	8.7	76.9
PVC-Cl5-TP-23.0%	268	61.5	9.1	71.4
PVC-F-TP-9%	300	63.8	9.3	81.2
PVC-F-TP-18%	300	63.0	8.0	78.1
PVC-F-TP-23%	300	63.3	5.3	73.5
PVC-F-TP-55%	295	63.1	5.3	54.3
PVC-F2-TP-4%	310	61.5	9.5	80.2
PVC-F2-TP-15%	305	61.5	9.1	77.5
PVC-F2-TP-35%	305	63.8	6.7	74.6
PVC-F5-TP-2%	307	59.2	12.5	85.2
PVC-F5-TP-12%	309	52.3	22.2	85.4
PVC-F5-TP-28%	310	47.2	28.9	82.6
PVC-F5-TP-44%	322	40.9	36.1	80
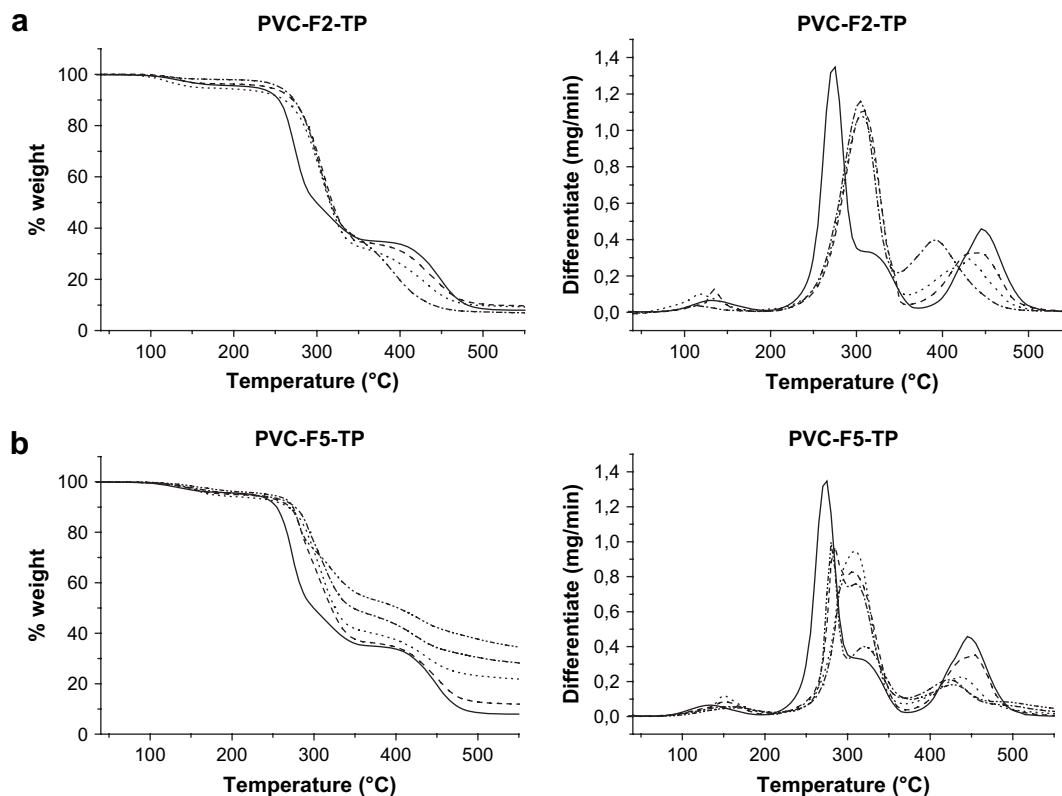
Fig. 6. Comparison of the thermograms of pure and modified PVC. (a) Pure PVC (—), PVC-F2-TP-4% (- - -), PVC-F2-TP-15% (···), PVC-F2-TP-35% (−·−·). (b) Pure PVC (—), PVC-F5-TP-2% (- - -), PVC-F5-TP-12% (···), PVC-F5-TP-28% (−·−·), PVC-F2-TP-43% (−··−··).

weight losses begin at temperatures between 20 and 50 °C higher than those of pure PVC being more stable the polymers the higher the degree of modification. Furthermore one can observe a tendency of a slight increase of the decomposition temperature with the number of fluorine atoms in the modifier (see Table 1 and Fig. 7).

The second weight loss process corresponds to the complete degradation of the polymeric system. However, in the cases of PVC-F-TP and PVC-F2-TP very little amount of residues remained at the end of the programmed temperature of

600 °C. In contrast, in the case of PVC-F5-TP, a considerable larger amount of residue remains at this temperature being larger the quantity of this residue the higher the degree of modification (in the PVC modified with 44%, resultant residue was >40% at 600 °C).

3.4. Glass transition temperature

Calorimetric measurements were performed in order to analyse the thermal properties of the modified PVCs and to study
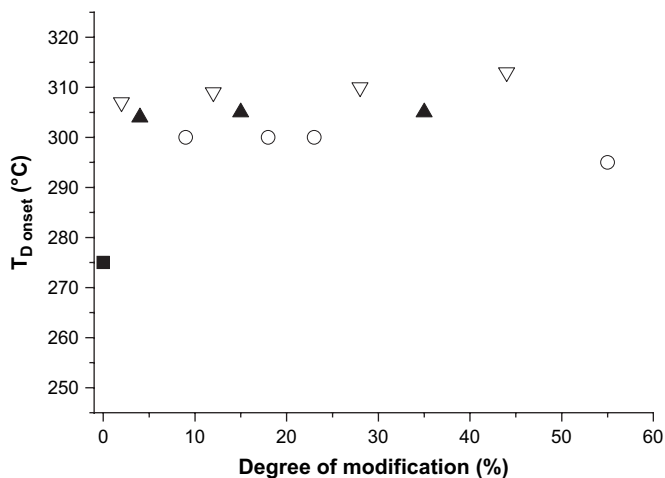

Fig. 7. Dependence of the degree of modification on the onset temperature of decomposition $T_{D\text{-onset}}$ of the first weight loss determined by TGA. PVC pure (■), PVC-F-TP (○), PVC-F2-TP (▲), PVC-F5-TP (▽).
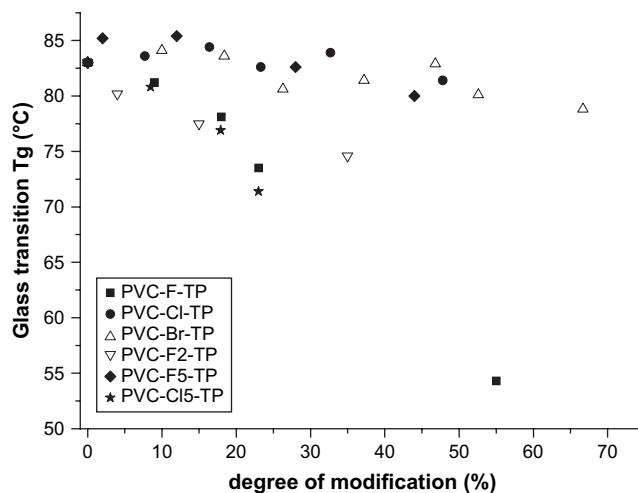

Fig. 8. Dependence of the glass transition temperature of modified PVC on the degree of modification.

the influence of the different halogen functionalities on T_g. The measured values are summarized in Table 1 and represented graphically in Fig. 8. As could be expected all modifiers act as plasticizing agents leading to polymers with lower glass transition temperatures as compared to pure PVC.

4. Conclusions

The present study shows that halogenated aromatic thiols can be used as selective modifiers for the substitution of chlorine in PVC. Reaction conditions can be found which avoid almost any elimination side reaction, and white products with high degrees of modification are obtained. The thermal stability of the modified polymers is significantly increased when the modifier contain fluorine atoms.

The modified polymers can be used as well defined model compounds. The efficiency of penta-chlorothiophenol modified PVC as non-migrating fungicide is now being studied.

Acknowledgements

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