

Modification of Polyvinylchloride in Solution or Suspension by Nucleophilic Substitution

S. MARIAN and G. LEVIN, *Department of Plastics Research, The Weizmann Institute of Science, Rehovot, Israel and Department of Chemistry, College of Environmental Science and Forestry, Syracuse, New York*

Synopsis

Nucleophilic displacement of chlorine from polyvinylchloride (PVC) suspended either in water or in solution can be achieved using a nucleophile such as a sodium thiolate ($R-S^-,Na^+$). The nucleophilicity of the salt increases if an ether linkage exists in a β position to the thiol group [$R-O-(CH_2)_2-S^-,Na^+$]. Addition of a solvent such as cyclohexanone (which is a good solvent for PVC) to the slurry increases substantially the degree of substitution. Elemental analysis shows that every chlorine displaced from the polymer is replaced by a thiolate group; thus almost no dehydrochlorination occurs. It is possible to obtain by this method a grafted polymer in which 33% of the chlorine atoms are replaced by the β -ether thiolate group. The resulting polymer behaves like an internally plasticized PVC. The higher the degree of substitution of chlorine, the greater the flexibility of the grafted polymer is. Other compounds, such as lauryl thiolate and diethyl dithiocarbamate, also were used as nucleophiles, the latter one resulting in a brittle crosslinked polymer whenever sulfur was above 2%. Grafting of polytetrahydrofuran from PVC also was achieved using tetrahydrofuran as solvent and silver-perchlorate as catalyst. The resulting flexible grafted polymer is believed to consist of longer chains of polytetrahydrofuran grafted from few displaced chlorine atoms along the PVC chain.

INTRODUCTION

Many commercial polymers such as polyvinylchloride (PVC) and polyvinylidene chloride have chlorine atoms attached to their backbone. The processing of such polymers is difficult, and the products obtained are very brittle and useless, unless additives are added to the raw polymers during the processing stage. However, in time, some of the additives diffuse out of the polymer matrix, leaving behind a polymer that cannot be of further use. In order to overcome such problems, the additives should be chemically grafted to the backbone of the polymers by partial substitution of the chlorine with other nucleophiles. The requirement from such a nucleophile as well as its ability to improve the properties of the polymer is to be a weak base and a strong nucleophile; under strong basic conditions, elimination of HCl from the polymer might occur. The nucleophilic displacement of the chlorine might be carried out on the polymer suspended in water or in solution. The former choice is more commercially attractive because the reaction could be carried out immediately after the polymerization stage.

Cationic grafting on PVC in solution was described by Kennedy et al.¹ The grafted polymers consist of a PVC backbone with polyisobutylene, butyl rubber, or polytetrahydrofuran (PTHF) branches. Catalysts such as di- or tri-alkyl-aluminum halides or silver triflate $AgOSO_2CF_3$ were used. It was assumed that

the above grafting will improve the mechanical properties of PVC, on the foreknowledge that addition of PTHF to standard recipes of PVC leads to resins with high impact strength and good resistance to discoloration.^{2,3}

Substitution of chlorine on PVC by functional groups such as dithiocarbamate, thiolate, xanthate, and dithiophosphate were carried out in aprotic solvents such as dimethylformamide (DMF) and hexamethylene phosphor tri-amide (HMPA) by Okawara.^{4,5} Preliminary experiments conducted by Okawara indicate that a lower percentage of substitution of the chlorine by azide and thiophenoxide groups may also occur, even on PVC suspended in water, if a cationic surfactant is added to the slurry. We would like to report in this paper on the modification of PVC using AgClO_4 in tetrahydrofuran (THF) and on the nucleophilic substitution of chlorine by thiolates and dithiocarbamates, carried out in slurry. From our experiments, it appears that the degree of substitution is affected by the addition of small amounts of solvent such as DMF or cyclohexanone to the slurry.

EXPERIMENTAL

Grafting PTHF on PVC in Tetrahydrofuran Using AgClO_4 as a Reagent

The grafted material was prepared by the addition of AgClO_4 (3.0 g) to a stirred solution of PVC (Grade 37 Frutarom Electrochemical Industries Co., Haifa, Israel) in THF (2 g of PVC in 50 g THF). The reaction was carried out at room temperature, under nitrogen for 48 h or until the solution became very viscous. The crude product was dissolved in THF and precipitated from methanol. This operation was repeated twice. The polymer thus obtained was dissolved in THF and films were prepared by casting the solution on an horizontal glass plate. IR analysis showed the combined spectrum of PTHF and PVC. The percent of chlorine in the grafted polymer was reduced from 56.8% to 26.0%. Repeated experiments with the same amount of PVC and a smaller amount of AgClO_4 (0.6 g) gave 39.4% Cl in the grafted polymers.

Nucleophilic Substitution of Chlorine on PVC Suspended in Water

A measured amount of suspension of PVC (grade 43, Frutarom, Electrochemical Industries Co., Haifa, Israel) in water (~35% solid content) was continuously stirred in the presence of an equivalent amount of nucleophile such as sodium thiolate or sodium dithiocarbamate. A solvent (equal weight to the solid content of the slurry) such as DMF or cyclohexanone was added to the slurry. Addition of the solvent was found to be essential for nucleophilic substitution to occur. After the reaction was completed, the suspension was separated and the polymer washed several times with distilled water, methanol, and ether. The resulting grafted polymer was dissolved in THF or chloroform and precipitated in methanol or petroleum ether. This procedure was repeated three times. Finally, the polymer was dried in a vacuum oven for 24 h. The sulfur and chlorine content of each polymer was determined.

Reagents

Sodium thiolates were prepared by reacting the corresponding thiol with a solution of sodium hydroxide in water. Sodium dithiocarbamate was used as received from BDH Chemicals Ltd. Solvents were also used as received without any further purification.

Synthesis of 2-(2'-Butoxyethoxy) Ethane Thiol

The thiol was prepared from the commercially available diethylene glycol mono-*n*-butylether [$\text{CH}_3(\text{CH}_2)_3\text{O}-(\text{CH}_2)_2\text{O}-(\text{CH}_2)_2\text{OH}$]. The hydroxy group was converted to the corresponding chloride by a procedure published by Blicke et al.⁶ The instructions were kept as published except that pyridine was added in a molar equivalent to the carbitol. The corresponding 2-(2'-butoxyethoxy) ethane chloride was obtained in 70% yield. bp 215°/760 mm. The 2-(2'-butoxyethoxy) ethane thiol [$\text{CH}_3(\text{CH}_2)_3\text{O}-(\text{CH}_2)_2\text{O}-(\text{CH}_2)_2\text{SH}$] was prepared using the thiourea method published by Wayne et al.⁷ The corresponding thiol was obtained after distillation (78°C at 2 mm Hg, 60% yield). Elemental analysis showed 17.2% S as compared to the theoretical 17.9%. The 90-MHz proton spectrum in CDCl_3 shows four different types of protons located at the following positions relative to TMS (see Fig. 1): (a) δ 0.914 (t) 3 protons; (b) δ 1.49 (m) 5 protons; (d) δ 2.73 (m) 2 protons; and (c) δ 3.59 (m) 8 protons. A different NMR spectrum was obtained in CD_3OD : (a) δ 0.924 (t) 3 protons; (b) δ 1.49 (m) 4 protons; (d) δ 2.63 (t) 2 protons; and (c) δ 3.54 (m) 8 protons.

In CDCl_3 as solvent, the NMR absorptions of the two α protons to the thiol group are split by the β protons and the S—H proton and therefore appears as a multiplet. (Maximum absorption at 2.73 ppm.) However, in CD_3OD the multiplet structure becomes a triplet as a result of deuterium exchange. The absorption of the SH proton is located around 1.49 ppm. This was concluded from the fact that the integrated area around 1.49 ppm changes from an area corresponding to five protons to an area corresponding to four protons when the solvent is changed from CDCl_3 to CD_3OD .

Elemental Analysis

Sulfur and chlorine content in the grafted polymer were determined by titration following combustion in a Schoeniger apparatus according to published procedures.^{8,9}

RESULTS AND DISCUSSION

Characterization of PTHF Grafted on PVC in Solution

The grafted material (26% Cl) with a maximum tensile strength of 200 Kg/cm² and maximum elongation at break of about 300% behaves like plasticized PVC. Unplasticized PVC is endowed with a good resistance to solvents. In contrast, a plasticized PVC has low resistance to solvents. Moreover, the plasticizer might leach out while in contact with the solvent. Therefore, it was interesting to measure the diffusion coefficient of different solvents through a PVC film in which the plasticizer is chemically bonded to the backbone of the polymer. The

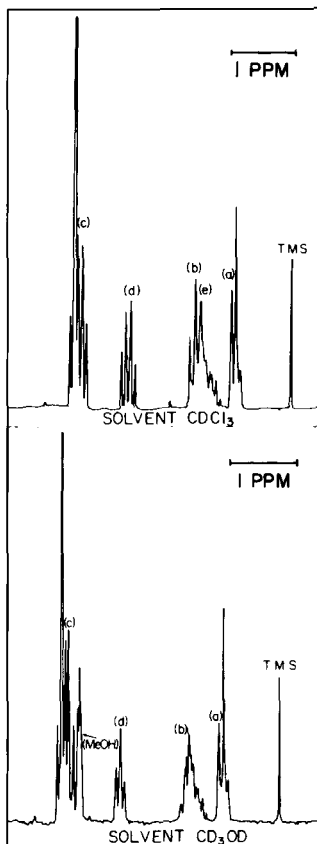
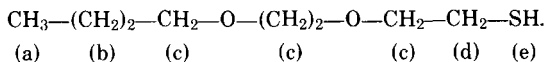


Fig. 1. 90-MHz proton spectrum of 2-(2'-butoxyethoxy) ethyl thiol in CDCl_3 and CD_3OD .



diffusion coefficient of different solvents through the film were measured using a procedure described elsewhere.¹⁰ A weighed strip of the grafted polymer was equilibrated with kerosin (fraction 236–290°C), ethanol, hexane, and toluene.

After equilibration at 30°C for 7 d, the films were weighed again and the rate of solvent evaporation was measured with a Perkin Elmer TGS-1 thermobalance. The diffusion coefficients of the above solvents in the grafted films were calculated using the diffusion equation for the region until 50% of the solvent was evaporated.

$$\frac{W_t - W_d}{W_s - W_d} = \left(\frac{16Dt}{\pi l^2} \right)^{1/2}$$

where W_t is the weight of film at time t , W_d is the weight of dry film, W_s is the weight of wet sample at $t = 0$, D is the diffusion coefficient, and l is the thickness of sample.

The PTHF grafted on PVC was also compared to the blend of the two homopolymers, i.e., PVC and PTHF. The last polymer was prepared by polymerization of THF using silver perchlorate and tertiary butylchloride as initiators. The diffusion coefficients of the solvents in the blended two homopolymers could not be measured because of the leaching out of PTHF. For example, after equilibrating with methanol for 7 d, the percent of Cl in the blended homopolymers increased from 28.2% Cl to 43% Cl. In contrast there was almost no change in the percent of Cl in the grafted polymer after all the equilibrated solvent was removed.

The diffusion coefficients of different solvents in the PVC with PTHF grafted on is given in Table I.

The diffusion coefficient of methanol in a methanol saturated film of PTHF grafted on PVC is higher by a factor of 2 than the diffusion coefficients of kerosin or hexane in the same film saturated with these solvents.

The result is expected on account of the higher plastification of the polymer backbone due to the interaction between methanol and the ether side chains of the polymer. This explains the higher diffusion coefficient for methanol as compared to hexane and kerosin.

Nucleophilic Displacement of Chlorine from PVC Suspended in Water

The grafted PTHF on PVC behaved like a flexible polymer. In this case the PTHF acts as an internal plasticizer. However, cationic grafting is unsuitable for commercial use because of the expensive catalysts used (silver salts). Moreover, removing the silver salts from the polymer is an expensive and tedious operation. Another disadvantage of this process is that the grafting proceeds in solution, which becomes very viscous if the concentration of the polymer increases over 10%. Therefore, in order to make the process of grafting commercially feasible, the grafting should be carried out on the polymer suspended in water.

Okawara⁵ reported that the degree of chlorine substitution on PVC suspended in water was 20% using thiophenoxide as nucleophile, and quarternary ammonium salt as phase transfer catalyst.

Experiments were carried out in our laboratory to find the optimal conditions for the nucleophilic displacement of chlorine from PVC suspended in water. Nucleophiles such as diethyl dithiocarbamate, lauryl thiolate and 2-(2'-butoxyethoxy) ethane thiol, lauryl mercaptan, *n*-butyl mercaptan, benzyl mercaptan,

TABLE I
Diffusion Coefficients of Different Solvents in PTHF Grafted on PVC (26% Chlorine)

Solvent	D (cm ² /sec)
Hexane	4.4×10^{-9}
Kerosin (fraction)	5.0×10^{-9}
Methanol	1.1×10^{-8}
Toluene ^a	—

^a Grafted polymer was swollen to about 70%.

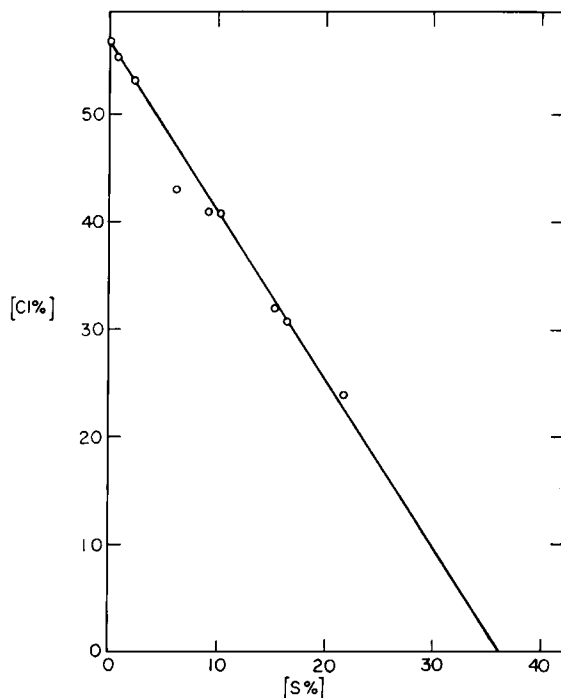
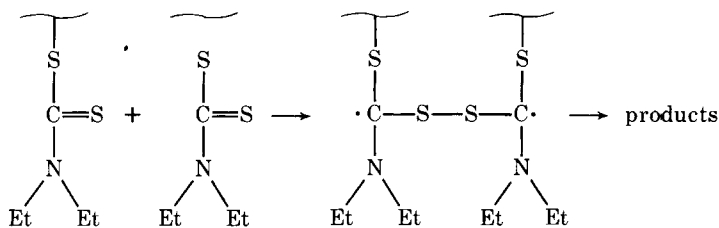


Fig. 2. Replacement of chlorine atom on PVC by dithiocarbamate group. (—) Theoretical relation between percent of chlorine and percent of Sulfur in the polymer; (O) experimental value.

and bis-(2-mercaptoethyl)ether were used in these experiments. The results indicated that a higher percentage of substitution occurs if a solvent for PVC such as DMF or cyclohexanone is added to the slurry.

Using the procedure mentioned above we studied the nucleophilic displacement of chlorine atom by a dithiocarbamate group. For example, mixing PVC suspended in water with sodium diethyl dithiocarbamate and cyclohexanone at 100°C for 24 h resulted in a polymer in which 33% of the chlorine was replaced by a dithiocarbamate group. The degree of substitution is increased with the reaction time and with the temperature. Elemental analysis of the resulted polymers showed in every case that one dithiocarbamate group replaces a chlorine atom, i.e., the percent of the sulfur on the polymer corresponds to the percent of chlorine that has been replaced (see Fig. 2). However, whenever the percent of sulfur on the polymer was higher than 2%, the polymer obtained was insoluble in common solvents. It seems that some side reactions occurred between the dithiocarbamate groups. We suspect the following:



Using lauryl thiolate as the nucleophile we also found the same agreement between the percent of chlorine lost from PVC due to substitution and the percent of sulfur gained due to grafting (see Table II).

We also compared the effect of the chain length of the thiol on the degree of substitution of chlorine on PVC suspended in water. Using *n*-butyl and *n*-lauryl thiolates as nucleophiles and DMF as swelling agent for the PVC, we found out that, after 24 h of reaction at 80°C, the degree of substitution was as follows: 10% of the chlorine atoms was replaced by *n*-butyl thiolate group as compared to 5% of chlorine atom that was replaced by lauryl thiolate group.

A substantial increase in the degree of substitutions was observed when bis-(2-mercaptoethyl)ether (HS—CH₂—CH₂—O—CH₂—CH₂—SH) was used as a nucleophile. On the basis of molecular dimension we expected a lower or in the best case equal reactivity to that of *n*-butyl thiolate. To our surprise we

TABLE II
Relation Between %Cl and %S in the Polymer Consisting of Lauryl Thiolate Grafted on PVC

Cl(%)	Theoretical S(%)	Experimental S(%)
40.00	4.15	3.99
44.76	2.85	2.31
46.85	2.40	1.57

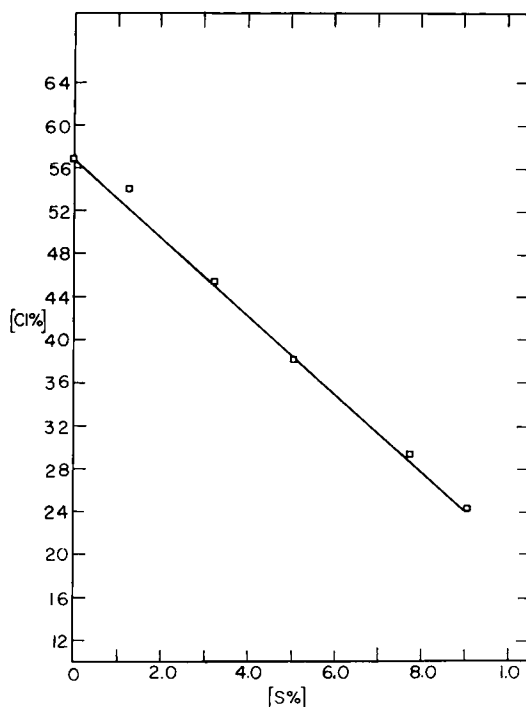


Fig. 3. Replacement of chlorine atom on PVC by 2-(2'-butoxyethoxy) ethyl thiolate. (—) Theoretical percent of S and Cl in the grafted polymer; (□) experimental percent of S and Cl in the grafted polymer. $[Cl\%]_{Th} = 56.8 - 3.62 [S\%]_{Th}$.

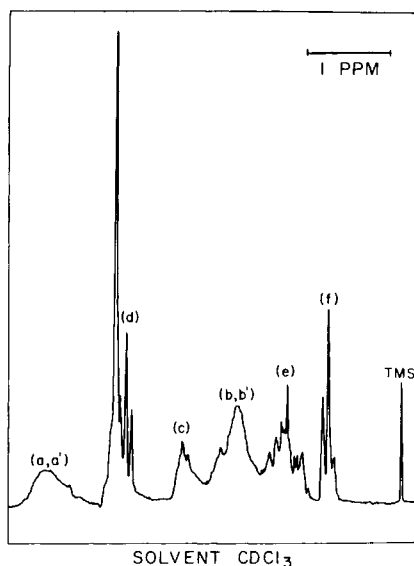
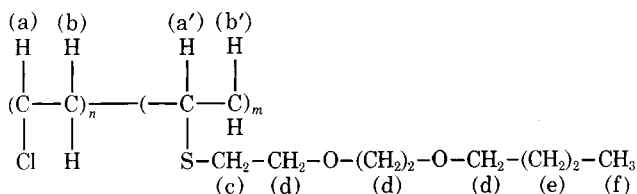


Fig. 4. 90-MHz proton spectrum of 2-(2'-butoxyethoxy) ethyl thiolate grafted on PVC.



found an increase in the reactivity of bis-(2-mercaptoethyl)ether as compared to *n*-butylmercaptan (taking into account that the former nucleophile is a bifunctional compound). The percent of sulfur on the grafted polymer was 18.32% as compared to 4.1% when *n*-butyl thiolate was used as nucleophile. The grafted polymer with pendent bis-(2-mercaptoethyl)ether groups was insoluble in common solvents, due to the bifunctionality of the nucleophile.

We suspected that the increase in reactivity of the thiolate is due to the exis-

TABLE III
Mechanical Properties of PVC and Thiolate Grafted on PVC^a

Polymer (cast film)	Elastic modulus (psi × 10 ⁵)	Stress at break (psi × 10 ³)	Maximum strain (in/in)
Unmodified grade 43 PVC	2.2	10.7	195
10% of chlorine on PVC displaced by CH ₃ (CH ₂) ₃ -O-(CH ₂) ₂ -O-(CH ₂) ₂ S ⁻	1.5	8.49	327
25% of chlorine on PVC displaced by CH ₃ -(CH ₂) ₃ -O-(CH ₂) ₂ -O-(CH ₂) ₂ S ⁻	0.003	—	>1200 ^b

^a Films were prepared by casting a 3% solution of the polymer in THF on a glass plate. The films were dried in a vacuum oven for one week at 55°C.

^b No break even at 1200% elongation.

tence of an ether linkage in a β position to the thiol group. This assumption was checked by synthesizing 2-(2'-butoxyethoxy) ethane thiol and using it as a nucleophile. The higher nucleophilicity of the above thio ether compound was clearly demonstrated by comparing lauryl thiolate and 2-(2'-butoxyethoxy) ethane thiolate. Under the same conditions (at 100°C and 24 h using cyclohexanone as swelling agent) the former nucleophile displaced 9% of the chlorine atom from the PVC suspended in water, as compared to 25% of chlorine atom when 2-(2'-butoxyethoxy) ethane thiolate was used as nucleophile. Moreover, 2-(2'-butoxyethoxy) ethane thiolate displaced 4% of the chlorine atom without using any swelling agent. On the other hand, under the same conditions, we could not detect any chlorine displacement when lauryl thiolate was used.

The results of the displacement of chlorine from the polymer by 2-(2'-butoxyethoxy) ethyl thiolate is given in Figure 3. From the data obtained we concluded that each chlorine atom displaced is replaced by a thiolate group. The calculation of the theoretical percent of sulfur on the polymer agrees with the experimental results. This implies that almost no elimination of hydrochloric acid occurred during the substitution. The IR spectrum of the 2-(2'-butoxyethoxy) ethyl thiolate grafted onto PVC shows, beside the characteristic absorptions of PVC bands, other bands that correspond to the ether functional group (1060–1080 cm^{-1} due to C—O stretch). NMR analysis of the grafted polymer (Fig. 4) shows a broad absorption of α and β protons attached to carbon backbone at 4.40 and 2.06 ppm, respectively. The protons attached to the thiolate residue are also present and they are more resolved than the backbone protons. As expected, the absorptions of the methyl protons at the end of the thiolate group are the most resolved. The assignment of the different protons was based on the NMR of the free thiol (see Fig. 1).

Mechanical Properties of 2-(2'-Butoxyethoxy) Ethyl Thiolate Grafted onto PVC

By increasing the degree of substitution of the chlorine on PVC by 2-(2'-butoxyethoxy) ethyl thiolate a flexible plasticizedlike PVC was obtained. The effect of the degree of substitution on the mechanical properties of the new polymer is given in Table III.

From Table III it is evident that the grafted PVC behaves like an internally plasticized polymer. The grafted polymer becomes more flexible as the degree of substitution increases.

In the future we intend to graft β thioethers with different functional groups, onto polymers containing chlorine.

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