Reactions of macroions leading to graft copolymers: crosslinking and grafting of PVC by carbanions*

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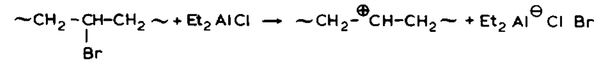
Carbanions react with Cl–CH PVC bonds to give graft copolymers. The selection of the bond reacting with anions is a function of several factors. Dianions predominantly attack those chains that have already been attacked and this leads to the crosslinking of only a fraction of the PVC macromolecules. The amount of the crosslinked fraction increases with increasing concentration and length of the crosslinking dianion and with decreasing temperature. The successive addition of dianions does not lead to a significantly increased amount of crosslinked PVC. No significant difference was observed between the crosslinking of PVC with simple dianions and those dianions prepared via the transformation of dications. PVC may be crosslinked both in solution and in suspension in alkanes. PVC macromolecules may be grafted efficiently only at relatively high concentrations of relatively long macroanions. Grafting carbanions may be obtained also from cationically polymerizing monomers through the transformation to anions of the growing centres. In this way PVC may be grafted by poly(tetramethylene oxide). Halogen substitution by an anion may be effected even in the presence of relatively low reactive silanolate ions, thus obtaining poly(dimethyl siloxane)-grafted PVC. Since carbanions are also capable of attacking ester groups, the interaction of dianions with PVC+PMMA solution gives rise to PVC-g-PMMA graft copolymers.

(Keywords: carbanions; crosslinking; grafting; poly(vinyl chloride); polystyrene; poly(tetramethylene oxide))

INTRODUCTION

Literature data[3] have suggested the possibility of grafting halogen-containing polymers by generating a carbocation on the chain to which the graft is being attached, e.g.:



$$\sim CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2\sim + Et_2AlCl \rightarrow \sim CH_2-\overset{\oplus}{C}H-CH_2\sim + Et_2Al^{\ominus}Cl\ Br$$

Scheme 1

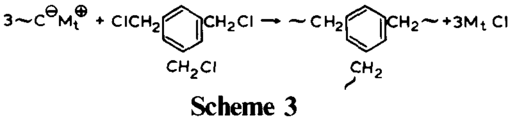
The branch grows on the carbocation via a cationically polymerizing monomer which is either free or in a form of complex with a suitable metallic compound[4].

For the majority of cases it seems, however, much more elegant to make use of carbanions for grafting onto polymers with carbon–halogen bond:

$$RR'CH^{\ominus}Na^{\oplus} + ClR'' \rightarrow RR'R''CH + NaCl$$

Scheme 2

The formation of star-shaped copolymers is an example of the above considered reaction[5,6]:



Scheme 3

Gregorian and Conway extended the versatility of reaction (2) to PVC grafting[7]. In this case active polystyryllithium macroions were used as a grafting agent. Mitsengendler *et al.*[8] have reported that the grafting performed in this way was not quantitative. They, of course, had to work at relatively high temperatures at which the carbanion character of the grafting polystyryllithium is already somewhat suppressed. One of the most interesting results of their study was the observation of selectivity of the grafting reaction as a function of a macroanion length and concentration. They observed a predominant carbanion reaction with the chains already containing grafts. Using anionic polystyrene with $K^{\oplus}$ as a counter ion, Gallot *et al.*[9] have also grafted PVC.

This technique could also be used for the preparation of some very interesting polymers which contain the grafts from anionically polymerizing monomers. Carbanions which are capable of grafting may be produced by the transformation of macrocations[1,2,10].

A satisfactory general analysis of mixtures of block or graft copolymers with corresponding homopolymers has still not been developed. The methods applicable to such mixtures usually separate the components according to the length and structure of individual chains. We have attempted to overcome this difficulty (knowing that we are not removing it completely) by modelling the grafting by crosslinking. When certain simplifying assumptions are made, then the monoanions should undergo the grafting reaction with PVC, while the dianions should lead to the formation of crosslinkages. It is relatively simple to determine the crosslinked fraction, which is represented by the proportion of polymer that is insoluble in a good solvent.

The interaction of carbanions with C–Cl bonds is accompanied by various side reactions.

In this paper, an attempt is made to broaden the observations made previously when examining the graft-

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* Previous papers in this series: see refs 1 and 2

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ing of styrene monoanions ($PS^{\ominus}$) to PVC. Further, the grafting behaviour was examined of monoanions formed from poly(tetramethylene oxide) cations ($PTHF^{\oplus}$) by the transformation to $PTHF^{\ominus}$ anions. Silanolate ions that are less reactive than carbanions were also a subject of study.

Carbanions also attack those polymers which contain an ester group in the side chain[7]. Thus, the reaction of the dianions with solutions containing PVC and poly(methyl methacrylate) (PMMA) yields graft PVC-g-PMMA copolymers.

EXPERIMENTAL

Materials

The solvents and other auxiliary compounds were of analytical grade, from Lachema, Czechoslovakia. The monomers: styrene from Kralupy; octamethylcyclotetrasiloxane (D_4) from Lachema–VCHZ Kolín; tetrahydrofuran (THF) from VEB Apolda, GDR, and the solvents were further carefully distilled and dried on a high-vacuum line[1]. The nitrogen for the experiments was dried and the oxygen removed by catalytic purification[1] (conc. O_2 and H_2O, resp., < 2 ppm). Other auxiliary materials used for the precipitation and extraction were used without drying (methanol, 2-propanol, etc.).

The preparation of the sodium salt of the α-methylstryene tetramer dianion ($^{\ominus}\alpha MeS^{\ominus}$; A) as well as that of the siloxonium dication is described elsewhere[11,12]. PVC, commercial Sicron 548-7M or 682 (average number molecular weight 36 100), was three times extracted with methanol at 323 K. As the weight of sample being extracted decreased less than 0.5%, this material was only dried on a high-vacuum line prior to further experiments.

PMMA was a commercial product of UMA Semtín; molecular weight 6.3×10^5. Apart from high vacuum drying it was used without further purification. The n-heptane solution of n-butyllithium (0.5% w/w) was a Texas Alkyls product. Mono-functional active polystyrene was prepared on a high-vacuum line through the reaction of butyllithium with styrene in THF at 263 K. The ratio of both components was selected in such a way that macroanions of the desired length and concentration could be formed.

Poly(tetramethyleneoxide) macrocations were prepared by THF polymerization with $ClO_4^{\ominus}\ {}^{\oplus}SiMe_2{-}O{+}SiMe_2{+}_5{-}O{-}Si^{\oplus}ClO_4^{\ominus}$ or $Me_3Si{+}O{-}SiMe_2)_6{-}OSi^{\oplus}Me_2ClO_4^{\ominus}$ as initiator at 263 K. The cations obtained were transformed to the corresponding macroanions[13-15] by reaction with the stoichiometric amount of $^{\ominus}\alpha MeS^{\ominus}$. The polymeric silanolate anions were prepared via D_4 polymerization induced by dry KOH at 423 K (2 h) or by using butyllithium at 298 K (30 days).

Instrumentation and apparatus

With the exception of the initiator dosage all operations connected with the preparation of macroions and grafting were carried out under high vacuum (10^{-2}–10^{-3} Pa). The initiator dosage was delivered using polyethylene capillaries and syringes. This arrangement removed the risk of contamination, thus enabling a simultaneous visual check of the diffusion rate of water and oxygen into the solution of coloured dianion. The amount of deactivated carbanions formed during the short period of opening the system (interactions with H_2O, O_2, CO_2, etc.) represented less than 1% of the overall dose[11]. Details concerning the reaction system have already been published[1,16]. The system is based on two or three interconnected vessels fitted with breakable seals. Each of these vessels could be attached to or sealed off from the vacuum line. The first ampoule contained the solution of the grafted polymer. In the second ampoule there was a solution of the cross-linking or grafting agent while a solution of the transforming diion, whenever necessary, could be placed in the third vessel.

The products of grafting were analysed by means of nuclear magnetic resonance (n.m.r.) spectroscopy (Tesla BS 487A, 80 MHz, 1.8 T), gel permeation chromatography (Waters Associates) and elemental analysis.

Procedure

The solution of active anions was added through a breakable seal to the THF solution of dried PVC (1.5 g PVC/20 cm^3 THF) under efficient stirring. After 1 h of reaction the apparatus was cut off, the product was precipitated, washed several times with methanol and dried to constant weight. The product was extracted with toluene when the grafts consisted of polystyrene or poly(tetramethylene oxide), or with n-hexane and toluene if the grafting was carried out by poly(dimethyl siloxane). The crushed material was maintained in suspension with the solvent for 8 h under constant stirring at 333 K. When micelles were formed in the system, the solid was separated either by decantation or by centrifugation. The solvent from the clear liquid phase was removed by evaporation and the solid residue was dried to constant weight. The insoluble solid phase was subjected to a further extraction by adding fresh solvent (60 cm^3) and stirring for another 8 h. Graft copolymers are agents influencing significantly the distribution of interfacial forces. Thus the separation of soluble and insoluble fractions was frequently a time consuming procedure requiring sometimes 25 or more cycles. Extractions were finished when less than 1% of the weight of the polymer was lost by extraction.

The extraction removed the copolymer from the grafting products, because the grafts used were soluble in toluene and osmotic forces were sufficient to maintain the graft macromolecules in solution. The portion insoluble in toluene, dried at laboratory temperature, contained (from n.m.r. spectra) only PVC with ~10% of toluene.

The simultaneous grafting of PVC and PMMA was carried out in a manner similar to that described above: to 1.5 g PVC and 1.5 g PMMA, dissolved in THF, $^{\ominus}\alpha MeS^{\ominus}$ was added. The product was extracted by ethyl acetate, which dissolves only PMMA but not higher molecular weight PVC.

RESULTS AND DISCUSSION

According to scheme (2), supported by the results of Gregorian and Conway[7], Mitsengendler *et al.*[8] as well as by Gallot *et al.*[9], the PVC grafting proceeds via chlorine substitution by the carbanion:

$$\sim CH_2-\underset{Cl}{CH}-CH_2-\overset{\delta+}{\underset{Cl}{CH}}-CH_2\sim + \overset{\oplus}{Na}{}^{\ominus}\!\sim \longrightarrow \sim CH_2-\underset{Cl}{CH}-CH_2-\underset{\wr}{CH}-CH_2 + NaCl$$

Scheme 4

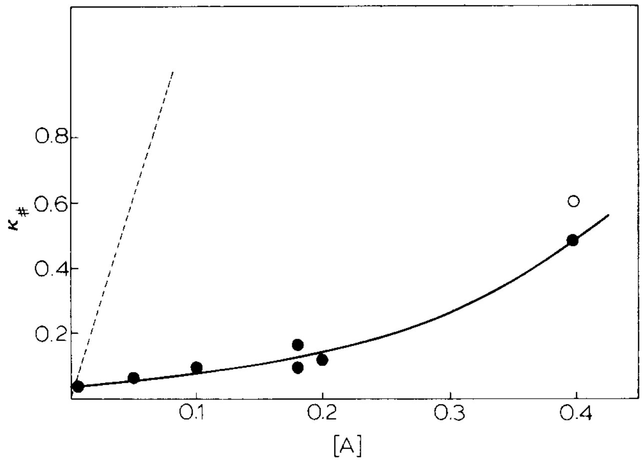
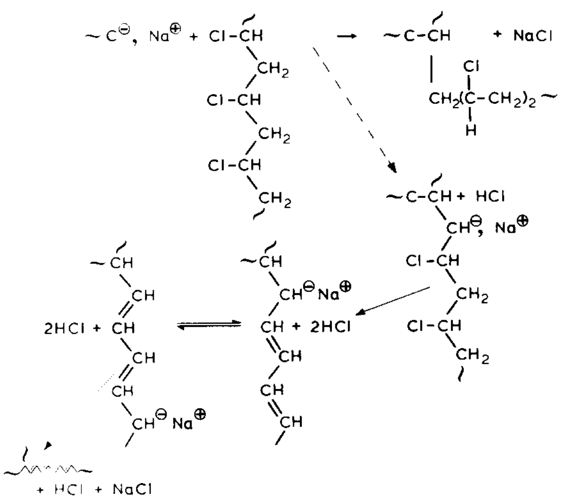


Figure 1 Dependence of the relative amount of PVC (insoluble in THF), $\kappa_{\#}$, on the concentration of α-methylstyrene tetramer dianion sodium salt [A]. Crosslinked PVC (1.5 g) dissolved in: (●): 20 cm^3 of THF; (○): 40 cm^3 of THF

Crosslinking of PVC

We have observed that during the interaction of PVC with the α-methylstyrene tetramer dianion, a gel of a slightly rosy colour was formed. The character of this coloration is indicative of the formation of sufficiently long PVC sequences containing conjugated double bonds and is indirect proof of dehydrochlorination.

Let us assume that a simple substitution, as described by equation (4), is accompanied by a small fraction of side and consecutive reactions:



Scheme 5

At a certain point in the development of conjugation, some groups of atoms may be more accessible to carbanion attack than others. This could account for the observed[8] 'selectivity' of grafting when carbanions reacted preferably with the chains that already contained some grafts.

Our experimental results are in accordance with this hypothesis: the amount of crosslinked fraction $\kappa_{\#}(=([\mathrm{PVC}]_0-[\mathrm{PVC}])/[\mathrm{PVC}]_0$; $[\mathrm{PVC}]_0$ and [PVC] stand for initial and actual concentration of non-crosslinked PVC molecules, resp.) depends on the concentration of crosslinking dianions (A) (see *Figure 1*).

Theoretically, n PVC macromolecules should require $2(n-1)$ of A molecules for total crosslinking. In this ideal case the dependence of $\kappa_{\#}$ on [A] should exhibit a character shown by the dashed line. The amounts of crosslinked fractions found experimentally differ considerably from an ideal case. The differences may be due to a predominating interaction of anions with the chains that have already been attacked. Only at relatively high concentrations of A does the fraction of crosslinked macromolecules becomes more pronounced. As shown in *Figure 2*, the amount of chlorine in the insoluble PVC fraction represents only about one half of the value expected when a simple substitution according to scheme (4) would have taken place. The chlorine content determined experimentally is not a function of length of the dianion undergoing the crosslinking. The lower chlorine content is in accordance with the formation of coloured polymers; the amount of chlorine eliminated is, however, somewhat surprising with regard to the amount of crosslinking dianion, the latter being by an order of magnitude lower. A substantial amount of the dianions should be neutralized by the HCl evolved. This is still to be clarified. Also the THF basicity should not be neglected since it can offset the acidity of HCl and its complexes. Another important factor is the kinetics of dehydrochlorination (the rate of this reaction after attack by an anion).

The influence of reaction conditions on the network formation

(*a*) *The influence of dianion length.* The amount of insoluble PVC was, under the conditions of study, always smaller than that expected when assuming a statistical control of the anion reaction with C–Cl bonds. It was also little dependent on the length of dianions, as shown in *Figure 3*. Because p increased only slowly with the growing weight of $^{\ominus}\mathrm{PS}^{\ominus}$ at constant dianion concen-

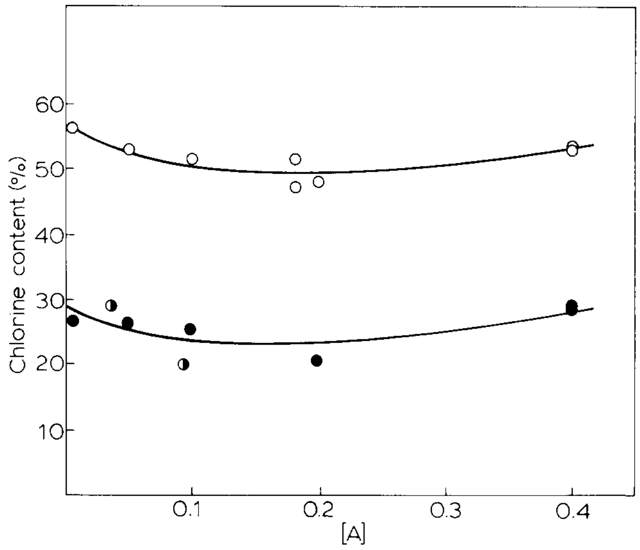


Figure 2 Chlorine content (in % w/w of theoretical value for intact PVC) in insoluble PVC fraction as a function of the crosslinking dianion concentration. (○): theoretical Cl content calculated from relationship:

$$\mathrm{Cl}_{\mathrm{theor.}}(\mathrm{mmol})=\kappa_{\#}\frac{1.5}{0.0625}-2[\mathrm{A}]=a-2[\mathrm{A}];$$

$$\%\,\mathrm{Cl}_{\mathrm{theor.}}=\frac{56.725}{a}\cdot\mathrm{Cl}_{\mathrm{theor.}}$$

Experimentally found chlorine content in samples crosslinked: (●) by A or by dianion $\mathrm{Na}^{\oplus}\,{}^{\ominus}\mathrm{PS}^{\ominus}\,\mathrm{Na}^{\oplus}$, whose molecular weight was (◑): 20 700; (⊖): 40 300

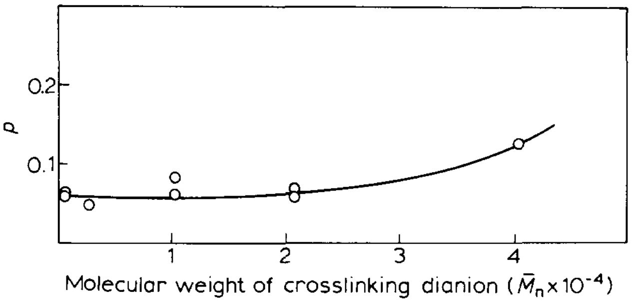


Figure 3 Dependence of the crosslinked fraction p on the molecular weight of crosslinking dianion. p = insoluble fraction of product (g)/sum of PVC and PS (A) weights entering the reaction (g). Under ideal conditions the quantity of dianion used should crosslink 43% of the overall amount of PVC undergoing the reaction (see (-----) in *Figure 1*)

tration, it may be stated that PVC chains already attacked by anions react more readily with other anions. But this tendency decreased with the increasing length of macroanions.

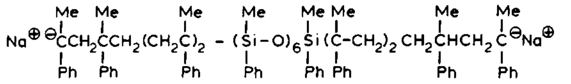
(*b*) *Influence of dilution and temperature of reactants.* The reaction of anions with PVC was rather fast. At 263 K the discoloration (i.e. reaction) of carbonions took place within seconds, even in a viscous medium. The contact of components should play an important role in the crosslinking process. In practice the influence of slight dilution was small. This was shown in a run during which the grafted PVC was diluted (point denoted as (○) in *Figure 1*); also the tests during which the grafting dianion was diluted with tetrahydrofuran support this assumption. The dilution with a greater THF volume causes a considerable decrease of a crosslinked fraction. The results are summarized in *Figure 4*.

With decreasing temperature of PVC–dianion interaction, the proportion of the crosslinked polymer increased (see *Figure 4*). At this stage it was difficult to decide if the effect was caused by greater resistance of carbanions to side reactions at lower temperatures or if it was a consequence of some other kinetic influence.

(*c*) *Successive and multiple addition of components.* An attempt was made to examine the reacting system further by adding the components successively. In some ampoules (fitted with a breakable seal) a 20 cm^3 volume of solution of PVC in THF (2.08 mmol dm^{-3}) was prepared for crosslinking. To this solution a calculated amount of A (0.108 mol dm^{-3}) was added. The sequence of component contact and other conditions are presented in *Table 1*. The interval between the individual additions was 15 min.

It follows from *Table 1* that further additions of PVC to the gel containing system have no significance in connection with the reactions leading to insolugle fractions. Even an additional small amount of A exhibited almost no influence upon the reaction yields. The observed values were constant within the experimental error also when a further small portion of A was added. Larger additions of A gave results which are ambiguous subject to increased experimental error. This was due to the presence of the initially formed gel, which makes the proper stirring of components very difficult. It seems, nevertheless, that A, added subsequently, reacts preferably with C–Cl bonds in the network. The reactivity increase of the attacked chains or the neutralization of carbanions by evolved HCl must be considerably important under these conditions.

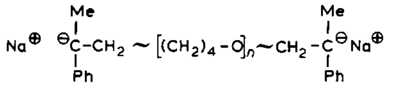
(*d*) *Crosslinking by dianions formed by the transformation of dications.* Transformation of polymeric cations to macroanions and subsequent reactions of the latter with halogenated polymers could yield both theoretically and practically important graft copolymers. We have tested the efficiency of this approach by measuring the amount and composition of the insoluble fraction formed via the PVC reaction with dianions obtained from dications. The siloxonium dication[12] reacts with a twofold excess of A giving rise to the corresponding dianion[10,16,17]:



$$Na^{\oplus}\,{}^{\ominus}\underset{Ph}{\overset{Me}{C}}CH_2\underset{Ph}{\overset{Me}{C}}CH_2(CH_2\underset{Ph}{\overset{Me}{C}})_2-(\underset{Ph}{\overset{Me}{Si}}-O)_6\underset{Ph}{\overset{Me}{Si}}(\underset{Ph}{\overset{Me}{C}}-CH_2)_2CH_2\underset{Ph}{\overset{Me}{C}}HCH_2\underset{Ph}{\overset{Me}{C}}{}^{\ominus}Na^{\oplus} \qquad \text{I}$$

Scheme 6

Tetrahydrofuran polymerizes when initiated by siloxonium cations[12] giving dications of poly(tetramethylene oxide) and macrocycles[18]. The dication may be, under suitable conditions, transformed by oligomeric dianions (e.g. by A) to give polymeric dianions[2,10,16,17]:



$$Na^{\oplus}\ {}^{\ominus}\underset{Ph}{\overset{Me}{C}}-CH_2\sim[(CH_2)_4-O]_n\sim CH_2-\underset{Ph}{\overset{Me}{C}}{}^{\ominus}Na^{\oplus} \qquad \text{II}$$

Scheme 7

Table 1 Successive and multiple addition of components

A In single doses (mmol)	Composition sequence of dosage	Insoluble portion %
0.036	PVC+A	4.8[d]
	(PVC+A)+PVC	5.6[a,c]
	(PVC+A)+PVC+A	6.1[b,c]
	(PVC+A)+PVC+A	8.2[b,d]
0.6	PVC+A	17.8[c]
	(PVC+A)+A	41.0[c]
	(PVC+A)+A+A	27.3[c]

[a] First PVC fraction
[b] Overall PVC amount
[c] 298 K
[d] 263 K

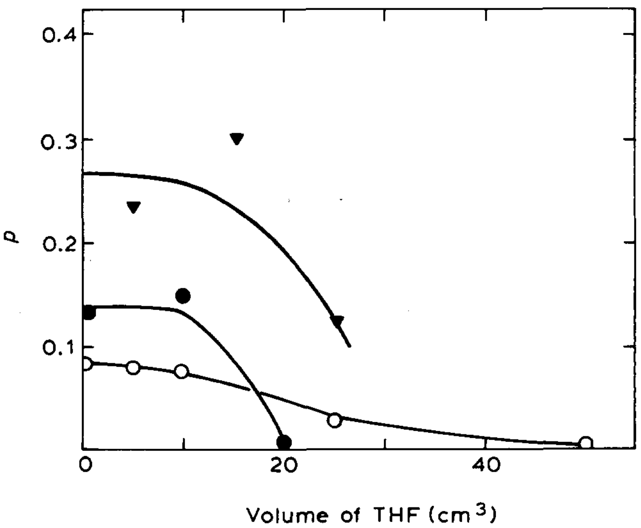


Figure 4 Dependence of the amount of crosslinked fraction p on amount of THF used for dilution of the crosslinking dianion. To 1.5 g PVC dissolved in 20 cm^3 THF, diluted dianion was added: 0.035 mmol of polystyrene dianion sodium salt (M_w = 20700) at 298 K (●); at 263 K (▲); 0.1 mmol A at 298 K (○)

Table 2 Crosslinking of 1.5 g PVC dissolved in 20 cm^3 THF using dianions obtained by dication transformation

Dianion			Crosslinked fraction	
Type	$\bar{M}_n$[a]	Amount (mmol)	%	Remark
I	1 446	0.0018	3.3	*b*
	1 446	0.009	0.6	*b*
	1 446	0.018	2.4	*b*
II	7 000	0.18	15.1	*c*
	18 500	0.09	6.0	*c,d*
	18 500	0.09	14.4	*c*
	18 500	0.09	14.1	*c*

[a] Excluding atomic weight of counter ions
[b] 298 K
[c] 263 K
[d] PVC/PTHF ≈96/4 mol/mol

Table 3 Crosslinking of 1.5 g PVC in 20 cm^3 n-heptane suspension produced by dianions

Dianion			Crosslinked fraction	
Type	$\bar{M}_n$[a]	Amount (mmol)	%	Remark
$^{\ominus}\alpha$MeS$^{\ominus}$	472	0.09	8.8	*b*
		0.09	13	*b*
$^{\ominus}$PS$^{\ominus}$	5 000	0.09	7.1	*c*
	20 100	0.09	12.6	*c*
	30 000	0.09	c6.4	*c*

[a] Excluding atomic weight of counter ions
[b] 263 K
[c] 298 K

(~ stands for the A residue, while the siloxonium initiator residue in the polyoxymethylene chain is not included in this formula). The results of dianion interaction of such species with PVC are summarized in *Table 2*.

At very low concentrations of the dianion (about 0.01 mmole) the results are not reproducible and the amount of crosslinked fraction is probably comparable with that connected via A bridges (see *Figure 1*). At higher concentration of the longer dianion the insoluble fraction is higher than it would follow from the curve in *Figure 1*. This difference is believed to be due to the differing length of polyoxymethylene bridges connecting the PVC chains.

(*e*) *Crosslinking of PVC in suspension.* From the practical point of view the possibility of PVC grafting in suspension might be of interest. It would circumvent the manipulation with large quantities of solvents and viscous solutions. We have thus attempted to model PVC grafting by carrying out crosslinking in n-heptane suspension. The results are given in *Table 3*.

In this case again the analysis of the product and the reproducibility of the synthesis were not satisfactory; the yield of crosslinking was, however, approximately the same as that obtained in solutions containing roughly the same amount of A (see *Figure 1*). The greater affinity of anions towards the chains already attacked predominates, under given conditions, over the statistical probability of contact with Cl–C bonds in various PVC molecules.

Grafting of PVC

The PVC crosslinking process induced by dianions serves as a good grafting model. This is corroborated by the dependence of the number of PVC grafted macromolecules upon the concentration of grafting $\sim S^{\ominus}Li^{\oplus}$ macroions (see *Figure 5*). Qualitatively, the function exhibits a character similar to that observed in the case of crosslinking. The quantitative differences are probably due to the differing lengths of the grafting anions. This follows also from *Figure 6*. At the lowest anion concentrations, various PVC molecules are being grafted; very soon the dominating character of branching sites becomes an important factor which enhances the anion reactions with the chains already grafted.

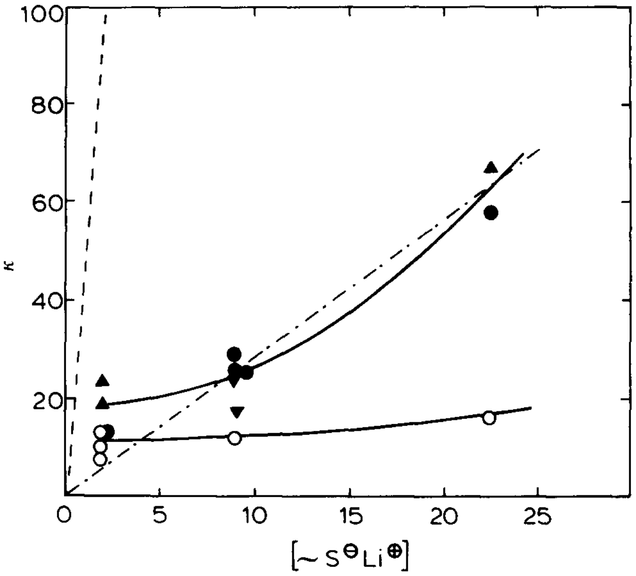


Figure 5 Dependence of grafted PVC fraction (in % on the initial amount) on the concentration of grafting polystyrene$^{\ominus}$Li$^{\oplus}$ macroanions of varying length (in mmol/dm^3). Molecular weight of polystyrene$^{\ominus}$Li$^{\oplus}$: (○): 2500; (▲): 10 100; (●): 20 100. Temperature of grafting 263 K. At perfectly uniform bonding of one graft (eighteen grafts) to one PVC macromolecule the dependence would exhibit the character of the broken line (-----)

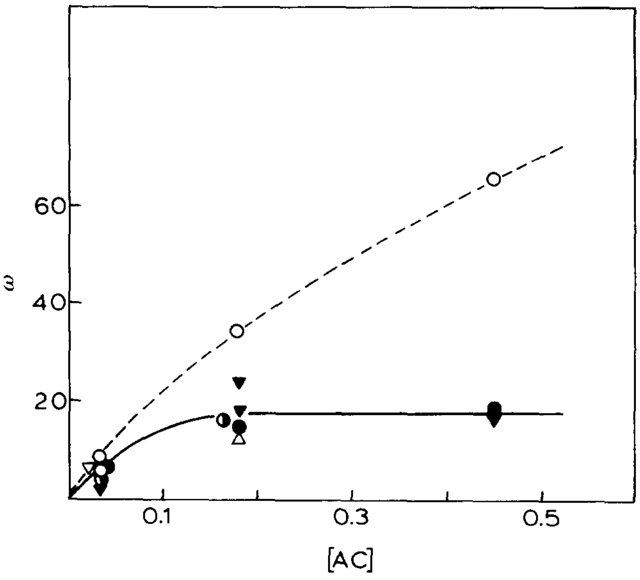


Figure 6 Dependence of maximum average number of grafts ω bonded to one PVC macromolecule on concentration of grafting $\sim S^{\ominus}Li^{\oplus}$ anions. Molecular weight $\sim S^{\ominus}Li^{\oplus}$: (○): 2500; (▲): 10 100; (●): 20 100; (△): 40 300. The grafting temperature was 263 K

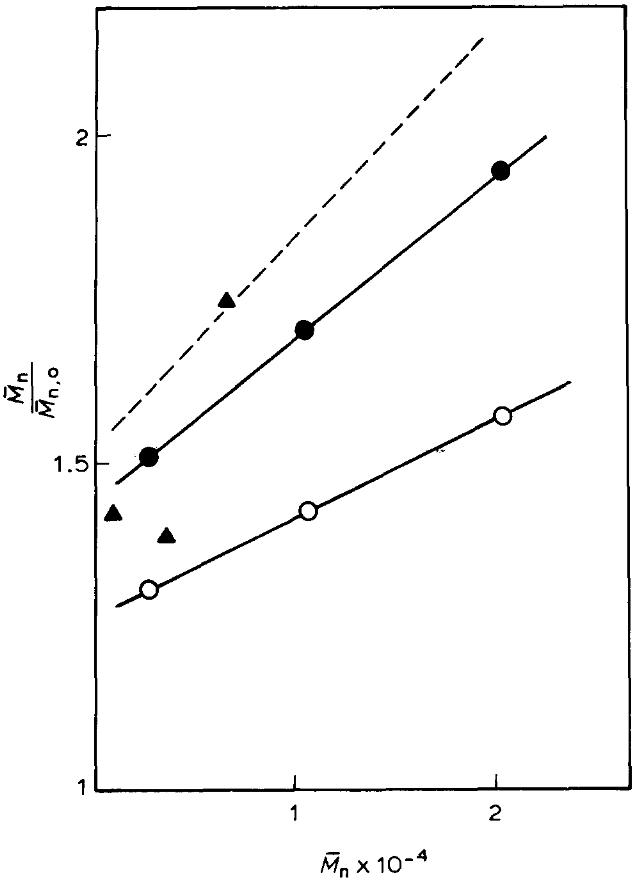


Figure 7 Dependence of molecular weight ratio of grafted product fraction insoluble in toluene (PVC after grafting and original PVC) on the length and concentration of grafting macroions. Macroanion concentration (mmol/dm^3); (○): 0.9; (●): 22.5; (▲): 27.0

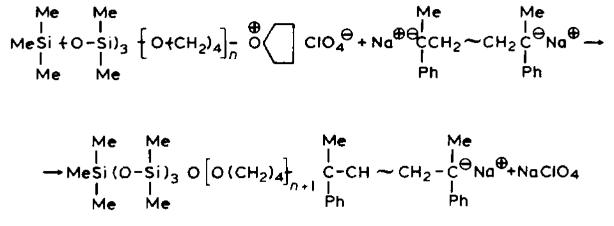
Table 4 PVC grafting by anions formed by macrocation transformation

Monocation (mmol/dm^3)	THF polymerization^a time (h)	THF polymerization^a $\bar{M}_n$	$^{\ominus}\alpha$MeS$^{\ominus}$ (mmol/dm^3)	PVC/THF^b	PVC sol.^{c}
9	72	8800	9	97/3	9.2
9	72	8800	9	98/2	24.4
9	144	17500	9	100/0	16.8

[a] 263 K
[b] Composition of an insoluble fraction after 6 to 8 extraction cycles in toluene at 333 K
[c] PVC transferred to solution in form of copolymer; % of the initial amount

The maximum average number of grafts on one PVC macromolecule — calculated from moles of grafted PVC and grafting PS$^{\ominus}$ — increases while the number of macromolecules being grafted remains practically constant. At higher concentrations of longer anions the average number of grafts on the PVC chains no longer increases. This means effectively that the number of grafted PVC molecules has to be increasing. All data so far described have been obtained on those grafted products that were soluble in toluene. The fraction insoluble in toluene (according to n.m.r. spectra of virtually pure PVC) has not, however, remained intact. This is manifested by the growth of its molecular weight with the increasing length and amount of grafting anions (*Figure 7*). The Cl content (*Figure 8*) in this fraction also decreases with the increasing anion concentration.

The anions capable of undergoing the reaction with PVC according to schemes (4) and (5) may also be obtained from cationically polymerizing monomers via the transformation of their growing centres to anions. We have tested the feasibility of this approach by the following experiment. An equimolar amount of $^{\ominus}\alpha$MeS$^{\ominus}$ was added after a certain time, to the THF, polymerizing on monocationic centres (Me$_3$Si–O$\sim^{\oplus}$SiMe$_2$ClO$^{\ominus}_4$) at 263 K.



Scheme 8

The anions thus formed were used for grafting to PVC. The product was separated by toluene extraction into soluble and insoluble fractions. The presence of poly(tetramethylene oxide) in the insoluble fractions could be excluded while PVC homopolymer could not be present in the soluble fractions. The weight of the insoluble fraction, lower than that of the initial PVC, was indicative of a partial transfer of PVC to solution — i.e. in form of the copolymer. The presence of both initial components in extracts was followed by n.m.r. The results are shown in *Table 4*.

The contact of the first anionic reactants with PVC leads to a fast appearance of turbidity while further macroanion fractions react both with the microgel and in solution. The proportion of the reactions cannot be

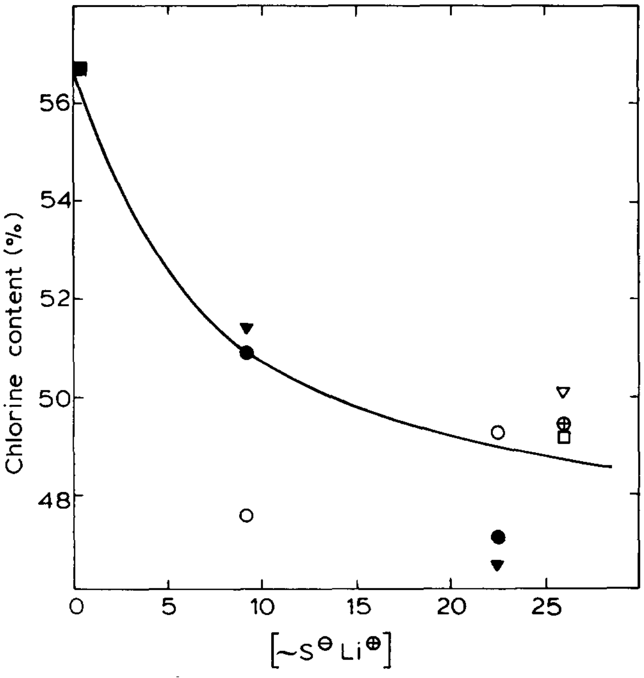


Figure 8 Dependence of chlorine content in toluene insoluble fraction (PVC) on concentration of grafting macroanions. (See legend to *Figure 4*.) Molecular weight of $\sim S^{\ominus}Li^{\oplus}$; (□): 840; (○): 2500; (⊕): 3400; (△): 6700; (▲): 10 100; (●): 20 100; (■): chlorine content in non-grafted PVC

Table 5 PVC grafting by polydimethylsilanolates

Macroanion				
Type	$\bar{M}_n$	Amount (mmol/dm^3)	Weight of product[a] (%)	Composition[b] PVC/PD
HOMe$_2$Si ~ Si–OK	2 500	10	112	95/5
BuOSi ~ Si–OLi	9 600	16	121	83/17

[a] Initial amount of PVC = 100%

[b] Fraction insoluble in toluene (mol/mol) (D = –SiMe$_2$O–)

Table 6 Formation of graft copolymers by reaction of α-methylstyrene dianion with PVC + PMMA[a] solution

$^{\ominus}$αMeS$^{\ominus}$ (mmol/dm^3)	Yield (g)	Insoluble fraction[b] (g)	Composition[c] PVC/PMMA
3.0	3.0330	1.7736	93/7
8.3	3.1166	1.8838	88/12

[a] To the solution of 1.5 g PVC + 1.5 g PMMA in 60 cm^3 of THF the $^{\ominus}$αMeS$^{\ominus}$ was added at laboratory temperature. The product was isolated and further treated after 216 h of interaction

[b] In ethyl acetate

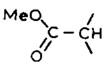
[c] Ethyl acetate-insoluble fraction

controlled by simple stirring. The scatter of experimental points is attributed to this factor.

The halogen in Cl–CH group may be substituted by even a less reactive (when compared to carbanions) silanolate ion. This was proved by grafting K or Li poly(dimethyl silanolate) to PVC. A multiple toluene extraction of product yielded both insoluble and soluble fractions. The n.m.r. examination revealed the presence of both components in both fractions; it follows, however, that PVC homopolymer could not be present in the soluble fraction while PD (where D ≡ –SiMe$_2$O–) homopolymer could not remain in insoluble fraction (*Table 5*).

The raw, non-extracted product exhibits the properties of an internally plasticized PVC. Even after several years no separation of components could be noted, even though the material has to contain some homopolymers besides the copolymer. This is indicative of a pronounced compatibilizing effect of PVC-g-PD.

Carbanions may be grafted not only onto PVC but also to poly(methyl methacrylate)[19]. The reaction rates of anions with Cl–CH are probably not too different from those with



since in the presence of dianions (e.g. $^{\ominus}$αMeS$^{\ominus}$) in the THF solution of PVC + PMMA, a copolymer is formed. This follows from *Table 6* which summarises the experimental results concerning the preparation of graft copolymers from PVC and PMMA through the interactions of the mixture with dianions. Both polymers were placed in contact with the dianion by employing breakable seal technique. The washed product was extracted by ethyl acetate. PVC homopolymer is insoluble in this solvent, in contrast to homopoly(methyl methacrylate). The presence of both components in both soluble and insoluble fractions was, however, confirmed by n.m.r. Also the fraction which was insoluble in ethyl acetate is easily dissolved (all but 2.4%) in THF. Thus almost no PVC-g-PMMA is crosslinked.

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