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Poly(vinyl chloride)-*g*-poly(2-methyl-1,5-hexadiene): PVC fitted with multiple allyl groups

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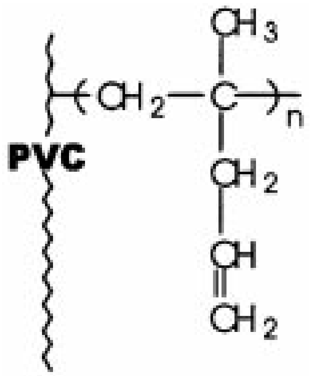
Summary

The objective of this research was to obtain poly(vinyl chloride) (PVC) backbone fitted with multiple allyl ($-CH_2CH=CH_2$) functions. We attained this objective by the carbocationic grafting of 2-methyl-1,5-hexadiene ($CH_2=C(CH_3)CH_2CH_2CH=CH_2$, MeHD) from PVC. Experimentally, grafting was mediated by adding Et_2AlCl to PVC/MeHD mixtures in methylene dichloride solutions in the -50 to -80 °C range. The structure and molecular weight of PVC-*g*-PMeHD were characterized by NMR spectroscopy and GPC, respectively. Our technique readily yields PVCs carrying up to ~8 allyl groups per backbone.

Introduction

The carbocationic grafting of various monomers, e.g., isobutylene, styrene, and other olefins from PVC was described years ago[1]. Very recently we have demonstrated the direct allylation of PVC by allytrimethylsilane by a cationic technique[2]. The number of allyl functions introduced by this method, however, was limited to ~1 allyl group per PVC chain because allylation proceeds only at the few weak chlorines present in PVC[2,3]. It occurred to us that the number of allyl groups per chain could be augmented by attaching poly(2-methyl-1,5-hexadiene) (PMeHD) branches to PVC, a polymer in which every repeat unit contains an allyl group:



This paper concerns cationic homopolymerizations of MeHD, followed by the grafting of MeHD from PVC by Et_2AlCl or $TiCl_4$, and the characterization of PVC-*g*-PMeHD.

Experimental

Materials. Chemicals were purchased from Aldrich, except as specified. Commercial PVC (Geon ® Resin 110x377, Mn = 36,600 g/mol) was supplied by The Geon Company. It was purified by precipitation from TBF into excess methanol, and dried in a vacuum oven at room temperature. Anhydrous methylene dichloride and 1,2-dichloroetnene (DCE), cumyl chloride (CumCl), diethylaluminum chloride, titanium chloride, and MeHD were used as received.

Polymerization of MeHD. Polymerization of MeHD was carried out in a stainless steel dry box equipped with a thermostated. bath under a dry nitrogen atmosphere. Into a series of large culture tubes (~ 75 mL) were placed charges consisting of MeHD (0.5 mol/L), CumCl (0.03 mol/L or 0.05 mol/L), and 20 mL CH_2Cl_2 or DCE depending on the temperature used. Polymerization was induced by the addition of Et_2AlCl ($5x10^{-2}$ mol/L in hexanes) to the solution. After 60 min, 5 mL methanol was added to the charges to terminate the polymerization. The PMeHD was precipitated with excess methanol, redissolved in hexane, and centrifuged for 1 hour to remove the aluminum oxide residues. The solvent was evaporated and the PMeHD was dried in a vacuum oven at room temperature.

Grafting of MeRD from PVC. Grafting of MeHD from PVC was carried out in the same equipment. A 200 mL flask equipped with mechanical stirrer, was charged with 80 mL CH_2Cl_2 solution of PVC (1 wt%), and was cooled to preselected temperature in the −50 to −80 °C range. MeHD (0.4 or 0.8 mol/L) and Friedel-Crafts acid ($TiCl_4$ or Et_2AlCl, $5x10^{-2}$ mol/L) were added, and the charge was stirred for 60 minutes. Methanol (~10 mL) was added to terminate the reaction. The PVC-*g*-PMeHD along with the PMeHD were precipitated with excess methanol, and extracted with hexane to separate the graft from hexane-soluble homopolymer. The PMeHD was dried in a vacuum oven at room temperature. The graft was redissolved in THF, centrifuged for 1 hour to remove metal oxide residues and dried in a vacuum oven at room temperature.

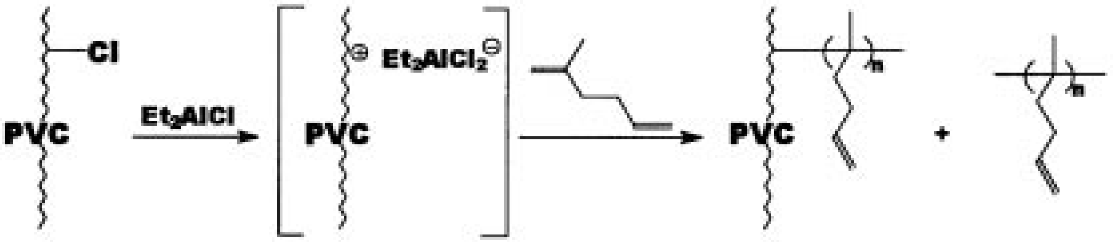
Characterization. ^1H NMR spectra were recorded by a Varian 300 spectrometer. Molecular weights were determined by a Waters high pressure GPC instrument as described[4]. The DP_n of the PMeHD branches was calculated by the following formula:

$$DP_n = \frac{^1H_{allyl}}{^1H_{PVC}} \times DP_{n,PVC} - 1.5$$

where $^1H_{allyl}$ indicates the allylic proton resonances in the 5.65-5.95 ppm range, $^1H_{PVC}$ gives the resonances at ~4.5 ppm associated with $-CH_2C\mathbf{H}(Cl)-$, and $DP_{n,PVC}$ is the number average of degree of polymerization of PVC.

Results and Discussion

The following Scheme serves to visualize our synthetic strategy:

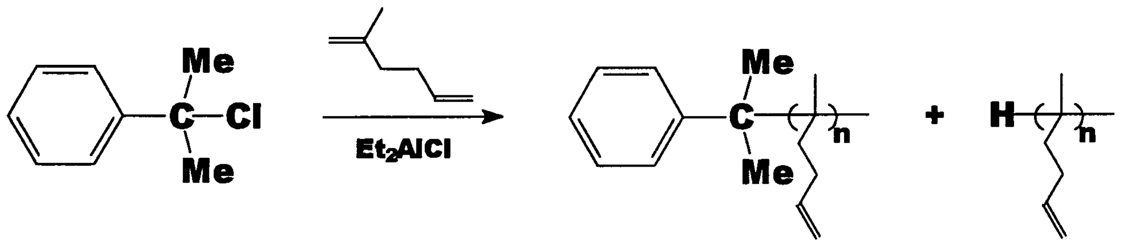


Scheme I. The grafting of MeHD from PVC.

Previous experience has amply demonstrated the intermediate formation of PVC$^+$ from conventional PVC in the presence of alkylaluminums, for example during the grafting of isobutylene (IB) from PVC[5]. The structural similarity between IB and MeHD is apparent. In view of the great cationic reactivity difference between the two double bonds in MeHD, we theorized that cationation of MeHD by PVC$^+$ will preferentially occur at the $CH_2=C(CH_3)$- function, particularly at low temperatures, and that the grafting of MeHD from PVC could be accomplished in this manner. We felt confident that conditions could be found for the synthesis of gel free PVC-*g*-PMeHD, in other words for selective grafting in the absence of crosslinking by the pendant allyl groups. Preparatory to grafting studies, we first carried out MeHD polymerization experiments mediated by the CumCl/Et_2AlCl initiating system. Guided by the results of these studies we succeeded in grafting from PVC low molecular weight PMeHD branches.

Homopolymerization of MeHD

Preparatory to grafting studies, we have investigated the homopolymerization of MeHD initiated by the CumCl/Et_2AlCl system (Scheme II). In these experiments we induced the polymerization of MeHD by the addition of Et_2AlCl coinitiator to the mixture of MeHD in CH_2Cl_2, or CH_2ClCH_2Cl solution (see experimental for details).



Scheme II. The homopolymerization of MeHD initiated by CumCl.

In line with previous experience[6], we anticipated the *in situ* formation of Cum$^+$Et$_2$AlCl$_2^-$, cationation of MeHD by the Cum$^+$, and consequently the incorporation of cumyl headgroups in PMeHD. In regard to tailgroups, we expected them to be Hs (or to a lesser extent C_2H_5 groups) because Et$_2$AlCl is known to terminate cationic polymerization by hydridation (or ethylation)[7]. However, no efforts were made to determine the nature of the endgroups in this research.

Table I. Homopolymerization of MeHD.

Temp. (°C)	Cumyl chloride ($\times 10^2$ mol/L)	Conv. %	Mn (g/mol)	Degree of polymerization
-30[a, b]	---	< 5	---	---
-30[a]	3.0	70	730	7.6
-30[a]	5.0	92	710	7.4
-50[c]	5.0	80	1010	10.5

a: solvent = DCE; b: control experiment; c: solvent = methylene chloride

Table I summarizes the results of three representative experiments together with a control experiment carried out in the absence of CumCl. Polymerizations proceeded readily and high conversions (70-92%) were obtained in 60 mins. According to molecular weight determinations, the number average degree of polymerization (DP$_n$) of the PMeHD were in the DP$_n$ = 7.5-10.5 range, which was deemed to be sufficient for the envisioned functionalization. The low DP$_n$ is most likely due to frequent chain transfer to monomer.

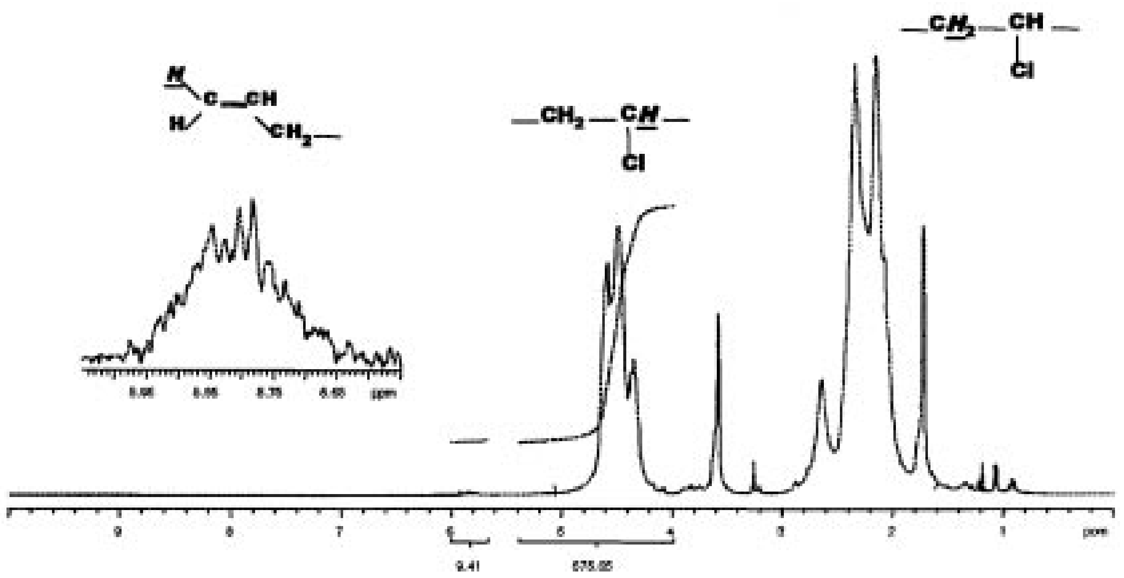


Figure 1. ^{1}H NMR spectrum of a representative PVC-*g*-PMeHD ([MeHD] = 0.8 mol/L, $TiCl_4 = 5 \times 10^{-2}$ mol/L, -80 °C).

Cationic Grafting of MeHD from PVC

Guided by the results of experiments with the CumCl/Et_2AlCl initiating system, we proceeded to commence grafting from studies. The grafting of MeHD from PVC was induced by adding Et_2AlCl or $TiCl_4$ cointiator to charges consisting of PVC and MeHD dissolved in CH_2Cl_2, cooled to a desired temperature (see experimental). The PMeHD was separated from PVC-*g*-PMeHD by exhaustive extraction with hexane, and its molecular weight was determined. The structure and composition of the hexane-extracted PVC-*g*-PMeHD were determined by ^{1}H NMR spectroscopy. Figure 1 shows the spectrum of a representative graft together with assignments. The characteristic resonance of the allyl function is in the 5.65-5.95 ppm range. However, the characteristic resonances for the abnormal structural units in PVC[8] also appears in this range. As demonstrated earlier[2], the abnormal structures in PVC contribute ~ 1.5 allyl groups. Since each repeat unit in PMeHD contains one allyl group, the number of allyl groups (after correcting for the allyl contribution by the abnormal structures) is equal to the number average degree of polymerization of MeHD. We have determined this quantity by integrating, and correlating the characteristic resonances of the allyl function (i.e., the terminal protons in $–CH_2CH{=}C\mathbf{H}_2$) with the resonances at ~ 4.5 ppm (associated with $–CH_2C\mathbf{H}(Cl)$-).

Table II. The effect of reaction conditions on grafting MeHD from PVC.

Temp. °C	Friedel-Craft acid	MeHD (mol/L)	Mn (PVC-*g*-PMeHD) (10^{-3} g/mole)	Total Allyl groups	DP_n PMeHD branch
-50	Et_2AlCl	0.4	36.5	5.0	3.5
-70	Et_2AlCl	0.4	37.0	6.4	4.9

-80	$TiCl_4$	0.4	36.7	8.7	7.2
-80	$TiCl_4$	0.8	36.8	9.6	8.1

Table II summarizes the results of grafting of MeHD from PVC. The fifth column in Table II specifies the total number of allyl groups in PVC-*g*-PMeHD. The sixth column shows the DP_n of the PMeHD branches (i.e., the difference between the number of allyl groups in grafts and virgin PVC). Evidently, under our experimental condition, PVC backbones carrying up to ~ 8 allyl groups can be prepared. The molecular weight of PVC-*g*-PMeHDs remained very similar to that of the PVC starting material, which suggests the absence of crosslinking.

The grafts were soluble in THF, methylene chloride, and 1,2-dichloroethane. The absence of gel indicates that the pendant allyl groups remained inactive during grafting and did not give rise to crosslinking. GPC traces of hexanes-extracted PVC-*g*-PMeHDs (not shown) indicated only one peak suggesting the presence of uncontaminated grafts.

Conclusions

Initiation of MeHD polymerization can be readily induced by PVC/Et_2AlCl or PVC/$TiCl_4$ combinations, and lead to grafts consisting of PVC backbones fitted with PMeHD branches: PVC-*g*-PMeHD. Experiments by the use of the CumCl as initiator in lieu of PVC have greatly facilitated the developing of conditions for efficient grafting. The structure and composition of PVC-*g*-PMeHD were analyzed by ^1H NMR spectroscopy. These grafts represent PVCs fitted with multiple allyl groups.

Acknowledgements.

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