Formylation of Pendant Aromatic Groups Attached to Linear Polymer Chains

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ABSTRACT: Polystyrene, poly(1-vinylnaphthalene), poly(9-vinylphenanthrene), and poly(1-vinylpyrene) undergo formylation on treatment with 1,1-dichloromethyl methyl ether and titanium(IV) chloride in carbon disulfide. Linear products were obtained in good yields. A high degree of substitution was observed in each case, except for polystyrene, in which only moderate functionalization could be achieved without appreciable cross-linking. The method is applicable to the formylation of both linear and cross-linked poly(vinyl aromatics). The degree of formylation of the polymers with condensed aromatic rings can be controlled by varying the molar ratio of reagents. The yields of linear products were reduced if very high M_w polymer was used due to the increased reaction times, leading to more cross-linked polymers. The formylated polymers reacted readily with malonitrile in the presence of piperidine.

Introduction

Formylation of pendant aromatic groups has been a key step in the functionalization of polymers. The aromatic aldehyde that results is highly reactive and can be used as a site for further synthetic manipulations. However, in contrast to its importance, there are few methods for the formylation of these polymers, and these all relate to cross-linked polystyrene and to formylation by multiple-step processes such as bromination, lithiation and then quenching with dimethylformamide,[1] or chloromethylation followed by oxidation using dimethyl sulfoxide.[2] No formylations of linear polymers have been reported.

Although *p*-formylstyrene is commercially available and can undergo free-radical polymerization to afford the linear *p*-formylstyrene polymer,[3] the syntheses of functional monomers with larger formylated aromatic substituents have not been reported. The preparations of such monomers appear to be difficult; therefore, the formylation of readily available poly(vinyl aromatics) is an attractive method of approach. The chief objective of the present study is to develop a general formylation method for such polymers. Most of our attention has focused on linear products, which may then be studied in solution or altered by further reactions. We are currently investigating some of the photochemically induced excited-state properties of these formylated linear polymers and their derivatives. Such photo- and electrochemical properties of polymers containing condensed aromatic chromophores are of much current interest.[4-6]

Experimental Section

Abbreviations. Formylated poly(1-vinylpyrene) (PVP), polystyrene (PS), poly(1-vinylnaphthalene) (PVN), and poly(9-vinylphenanthrene) (PVPh) are abbreviated PVP–CHO, PS–CHO, PVN–CHO, and PVPh–CHO, respectively. Meanwhile, P–CHO is designated as the general term for these types of polymers. The reaction products of formylated polymers with propanedinitrile are similarly abbreviated to PVP–CH=C(CN)$_2$, PS–CH=C(CN)$_2$, PVN–CH=C(CN)$_2$, and PVPh–CH=C(CN)$_2$, accordingly. In like manner, P–CH=C(CN)$_2$ becomes the general term for this class of polymers.

General Methods. Gel permeation chromatograph spectra were obtained by a standard method,[7] with a Water Associates Model M 6000A HPLC with Model U6K injector and Perkin-Elmer LC-75 spectrophotometer detector. The UV detector was set at 330 nm for PVP–CHO, 280 nm for PVPh–CHO and PVN–CHO, and 254 nm for PS–CHO. All the molecular weights are based on standard polystyrene samples in THF and are not corrected. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR with CHBr$_3$ as solvent, and ^{1}H NMR spectra, on a Varian VXR 300 spectrometer running at 300 MHz using Me$_4$Si as the internal reference. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Styrene was purified by the standard method, and dry toluene was obtained by refluxing with metallic sodium for 1 h before distillation.

Preparation of Polymers. 1-Vinylpyrene (mp 88–89 °C),[8] 1-vinylnaphthalene [bp 95–96 (4.0 mm)],[9] and 9-vinylphenanthrene (mp 34–36 °C)[10] were prepared by the Wittig reaction starting from their corresponding aldehydes. Their polymerizations were carried out at 60 °C under N$_2$ in dry toluene with AIBN as initiator. The polymers were precipitated from solution by the addition of ethanol. The residual monomer was removed by refluxing with ethanol in a Soxhlet overnight. It was found that poly(1-vinylpyrene), when initially precipitated from its polymerization solution, could contain as much as 20% residual monomer.

Formylation of Polymers. All the polymers were formylated by the same general procedure. A typical formylation of PVP is given as the example. 1,1-Dichloromethyl methyl ether (0.94 mL, 10 mmol) was added to a solution of PVP (1.14 g, 5.0 mmol) in CS$_2$ (100 mL). Titanium(IV) chloride (1.1 mL, 10 mmol) was then injected and the yellow solution darkened immediately. The mixture was stirred at room temperature for 1 h and was decomposed by the addition of 1 N HCl (50 mL). The CS$_2$ was removed by distillation, and the polymer was filtered off and washed with water, ethanol, and finally ammonia. The crude PVP–CHO was further purified by reprecipitation from its clear chloroform solution with ethanol. The final product (1.17 g) was obtained as a pale yellow powder after drying in a vacuum oven at 60 °C overnight.

Reaction of Formylated Polymers with CH$_2$(CN)$_2$ (Knoevenagel Condensation). In a typical reaction, malononitrile (0.1 g, 1.5 mmol) was added to a formylated polymer (0.1 g, <1.0 mmol) in chloroform (25 mL), followed by the addition of a catalytic amount of piperidine. The reaction mixture was stirred at room temperature for 1 h and the precipitated polymer filtered off. If the polymer did not precipitate, 95% ethanol was added to induce the separation. The crude polymer was purified by refluxing with acetone in a Soxhlet overnight.

Results and Discussion

Cross-linking during reactions of linear polymers is a common phenomenon due to the short separation between two functional groups in the polymeric chain. In many cases, the mechanism of the cross-linking reaction remains unknown. Only cross-linked P–CHO was obtained when the polymers, **1a–d** in Scheme I, were formylated by published methods.[1,2] Direct lithiation of the polymers, except in the case of PS, was not possible since poly-

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Table I
Results of Polymer Formylation

polymer	$M_w \times 10^{-3}$	M_w/M_n	IR(C=O), cm^{-1}	degree of formylation,[a] %	yield,[b] %
PS-CHO	16.5	1.22	1695	27	45
PS-CHO (cross-linked)[c]			1695	~20	
PVN-CHO	11.2	1.06	1678	56	65
PVPh-CHO	11.8	1.22	1684	45	78
PVP-CHO	15.2	1.23	1672	58	92

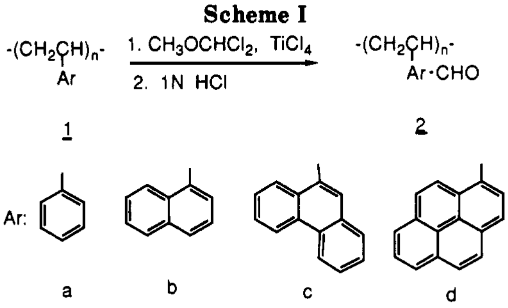
[a] Determined from ^{1}H NMR except for cross-linked PS-CHO, which is estimated from its IR spectrum. [b] Based on the recovered linear products. [c] Polystyrene-2% divinylbenzene copolymer beads (200-400 mesh).

Table II
Solubility of Formylated Polymers[a]

	solvents						
polymer	$CHCl_3$	THF	DMF	DMSO	$C_6H_5CH_3$	C_6H_5Cl	CS_2
PS-CHO	Y	Y	Y	P	Y	Y	Y
PVN-CHO	Y	Y	Y	P	Y	Y	Y
PVPh-CHO	Y	Y	Y	Y	Y	Y	Y
PVP-CHO	Y	P	Y	N	N	N	Y

[a] Y, soluble; N, insoluble or sparingly soluble; P, partially soluble. Conditions: 0.05 g of polymer in 5.0 mL of solvent at room temperature.

Scheme I



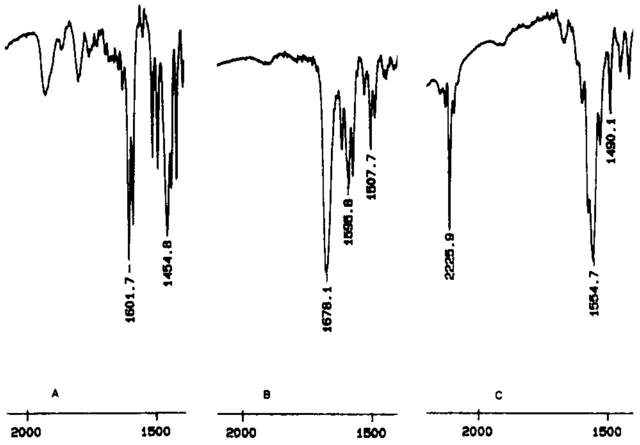


Figure 1. IR spectra of PVP (A), PVP-CHO (B, 71% substituted); PVP-CH=C(CN)$_2$ (C, derived from B).

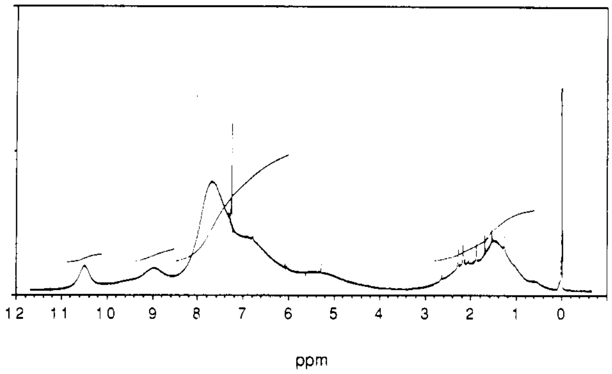


Figure 2. ^{1}H NMR of PVP-CHO (49% substituted) in $CDCl_3$ at room temperature.

(vinyl aromatics) are not soluble in hexane.[11] Treatment of the brominated polymers with phenyllithium or butyllithium resulted in insoluble products. The oxidation of chloromethylated polymers (P-CH_2Cl) was also not useful due to the difficulty in preparing linear P-CH_2Cl with appreciable amounts of substitution. The Vilsmeier reaction,[12] another frequently used method for the formylation of aromatics, failed to formylate the polymers at room temperature and decomposed them at higher temperatures.

The use of dichloromethyl butyl ether and titanium(IV) chloride as a formylating reagent for coronene has been reported.[13] The high reactivity of the reagent, and the easy hydrolysis of the dichloromethyl substituent introduced, suggested this to be a potential method for the formylation of the polymers (Scheme I). Evidence that the formylation of our polymers has indeed taken place is as follows. Strong carbonyl absorption bands (ranging from 1670 to 1700 cm^{-1}) and broad aldehyde proton peaks (centered at 10.5 ppm), are observed in the IR spectra and the NMR spectra, respectively, of all the products. These absorptions are not present in the starting polymers. The formylated polymers react with $CH_2(CN)_2$, and the IR spectra of these products show intense nitrile absorptions around 2230 cm^{-1} (Figure 1). All polymer products also give good elemental analysis results for their corresponding structures.

The ^{1}H NMR spectrum of a PVP-CHO sample, prepared by the conditions exactly described in the Experimental Section, is illustrated in Figure 2. The resonance around 9 ppm is the proton from the pyrene unit, which is observed as a doublet at 8.87 ppm in pyrene-1-carboxaldehyde.

The polymers in Table I, with the exception of PS, were obtained under the conditions described in the Experimental Section. Formylation of PS was carried out with a longer reaction time. The degree of formylation of the polymers given in Table I is defined as the percentage of repeating mono- or polycyclic aromatic units that are formylated. This percentage was estimated from the comparison of the integrations of the aldehyde and aromatic protons. Polymers bearing condensed aromatics can be functionalized to a very high degree without crosslinking by increasing the ratio of reagents. In other words, the degree of functionalization for condensed aromatic polymers can be controlled. As is indicated in Figure 3, the degree of substitution of PVP could be varied by the

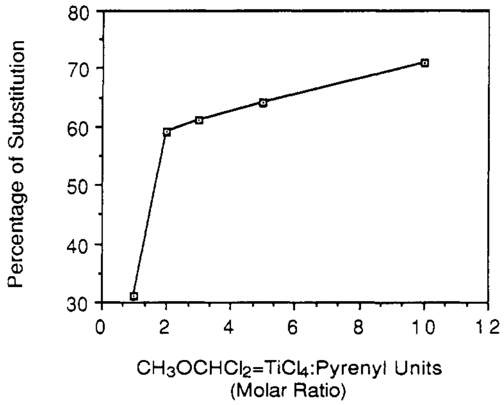


Figure 3. Dependence of PVP substitution on the amount of reagents used.

use of different molar ratios of reagents, although the overall yield was found to decrease with an increasing degree of substitution. In the case of PS, attempts to raise the degree of substitution by increasing the reaction time or the ratio of the reagents resulted in cross-linking of the polymer. The relatively low substitution of PS may be accounted for by the low reactivity of the phenyl group toward electrophilic substitution, relative to the reactivities of the larger aromatic systems. Highly substituted PS-CHO can alternatively be obtained by the polymerization of *p*-formylstyrene.[3] Notably, the yields in Table I increase with the size of the aromatic functional group.

Moderate molecular weight polymers were used in the present study, as is shown in Table I. The effect of molecular weight was investigated by using PS. The formylation of PS becomes more difficult as the molecular weight increases. The yields of the formylated PS decrease with higher molecular weight samples due to the longer reaction times required, which lead to more cross-linked product. However, for the polymers with condensed aromatic groups, high molecular weight is better tolerated in their formylation reactions than that for PS. The high reactivity of the condensed aromatic ring allows high molecular weight samples to be formylated in times sufficiently short to avoid the cross-linking reaction. An example of this was that a reasonable yield (78%) of highly substituted PVP-HCO was prepared in a few minutes using a molar ratio of CH_3OCHCl_2–$TiCl_4$–pyrene units of 10:10:1. However, PS of comparable molecular weight under the same conditions was formylated only if it was reacted for a much longer time.

Experimental results indicted no sign of polyfunctionalization. The PVP with the highest degree of substitution shows only one carbonyl absorption in its IR (see Figure 1), and the UV spectrum of this polymer is very close to that of the pyrene-1-carboxaldehyde except the residual pyrene absorption around 350 nm. The ability of the aldehyde group to deactivate and the steric hindrance from polymeric chain apparently preclude the introduction of a second substituent under the present mild reaction conditions (room temperature, 1 h).

The solubility characteristics of the formylated polymers are listed in Table II. The PVP-CHO listed there is the 58% substituted sample from Table I. For the PVP-CHOs in Figure 2, the general solubility is in reverse order of the degree of substitutions. For instance, a 31% formylated sample of PVP-CHO is soluble in nearly all the solvents listed in Table II whereas the 71% substituted sample only in CS_2 and $CHCl_3$. The appreciable solubility of these formylated polymers in organic solvents makes them highly useful intermediates for further modifications and for property studies.

Significantly, this formylation method works well not only for linear but also for cross-linked polymers, as is illustrated by the result of cross-linked PS (Table I). Besides the advantage that the PS-CHO is obtained in one step, as compared with the reported multiple-step preparation,[1,2] it is reasonable to assume, from the results of linear polymers, that the product has undergone little additional cross-linking. Therefore, PS-CHO prepared in this way should possess a similar degree of cross-linking and porosity as that of the starting material, and the aldehyde group should react rather completely in its further reactions. It is well-known that the inaccessibility of functionality created by additional cross-linking reduces its reactivity.

All the P-CHOs reacted readily with malononitrile in the presence of a catalytic amount of piperidine. The completion of the reactions was indicated by the disappearance of the strong carbonyl absorption band at 1670–1700 cm^{-1} and the presence of 2230-cm^{-1} nitrile absorption in the IR spectra of the products. The $P-CH=C(CN)_2$ polymers are colored due to the extended conjugation. With the presence of the interesting charge-transfer absorption band centered at 450 nm the UV spectrum of a highly substituted $PVP-CH=C(CN)_2$ is very similar to that of the 1-pyrenylmethylenepropanedinitrile.[14]

Conclusion

The use of 1,1-dichloromethyl methyl ether and titanium(IV) chloride in carbon disulfide has proved to be a very good method for the formylation of both linear and cross-linked poly(vinyl aromatics), especially for polymers bearing condensed aromatic substituents. Other reported methods are not suitable for the formylation of linear polymers due to the occurrence of cross-linking during the reactions. The mild reaction conditions and the short reaction time of the present method minimize the formation of cross-linked polymers.

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