Chlorination of Poly(vinyltoluene) by Electrolysis in an Organic/Water Suspension System

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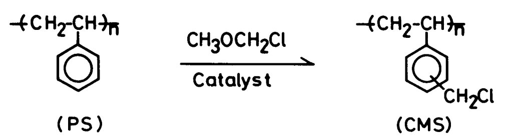
Synopsis. Chlorinated poly(vinyltoluene) was synthesized by controlled-current electrolysis of poly(vinyltoluene) in a suspension system consisting of aqueous and organic solutions. A high Cl-content polymer, in which Cl was introduced to the methyl group and the main chain, was obtained without changes in the molecular-weight distribution of the polymer.

Chlorinated poly(vinyltoluene) (C-PVT) and its derivatives are promising materials as sensitive nega-type microresists which cross-link under electron beam or X-ray irradiation.[1—3] Among them, poly[(chloromethyl)styrene] (CMS) has been synthesized by the chloromethylation of polystyrene (PS)[4] (Scheme 1). This method, however, involves a rather complicated procedure and tends to change the molecular-weight (MW) distribution of the product polymer.[3] On the other hand, a direct chlorination of poly(vinyltoluene) (PVT) by Cl_2 gas or thionyl chloride with some catalysts also yields C-PVT.[5] However, with this method it is difficult to control the Cl content and the substitution position in the polymer. We have found a simple process for introducing Cl to the methyl group as well as to the main chain of PVT which involves electrolysis.



Scheme 1.

There has been much work concerning the electro-halogenation of aromatic compounds with low molecular weights,[6] but little is known about the electro-halogenation of macromolecular compounds.[7] The principal reason for this is the difficulty in choosing a homogeneous electrolyte system. In this work, we have employed a suspended system consisting of an organic solution and an aqueous electrolytic solution.

Experimental

The starting PVT was prepared at Toyo Soda Manufacturing Co. Two kinds of polymers were used; one was a mixture of *m*- and *p*-isomers ($\overline{Mn} \simeq 40000$: PVT-I), and the other consisted of *p*-isomer only ($\overline{Mn} \simeq 170000$: PVT-II). The polydispersivity ($\overline{Mw}/\overline{Mn}$) was about 1.1 for both polymers. An electrolytic synthesis was conducted in a suspension system consisting of aqueous and organic solutions. The aqueous phase contained an acid, HCl, which acted as both a supporting electrolyte and a Cl source. The organic solvent was dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), or benzene (C_6H_6), which dissolved the substrate PVT. The electrolytic cell was a normal beaker-type, one-compartment cell (volume: $\simeq 50$ cm^3). The anode was a platinum wire (surface area: 3.5 cm^2), and the cathode was a platinum sheet (surface area: 6.5 cm^2). Controlled-current electrolysis was carried out with vigorous stirring of the solution using a magnetic stirrer while water-cooling the cell (16°—20 °C). The electric charge was normally 2.41×10^5 C (2.5 F) per mol of monomer. Such a charge ideally enables 1.25 atoms of Cl per monomer unit to be introduced to PVT.

The product polymer, separated from the organic phase, was purified by reprecipitation. No attempt was made to exclude light during the electrolysis, but the isolated products were stored under an Ar atmosphere while shielding the container from light. The Cl content in the product was determined by an elemental analysis, and the MW distribution of the polymer was estimated by gel permiation chromatography (GPC). The chlorinated position in the product polymer was determined by ^{1}H NMR spectroscopy (solvent: $CDCl_3$, standard reference: TMS).

Results and Discussion

Table 1 shows the results of the electro-chlorination of PVT in organic/water suspension systems. An estimation of the MW distribution of the products was based on the shape of the GPC curves, and is qualitatively described in the last column of Table 1 (symbols A, B, and C). The values of $\overline{Mw}/\overline{Mn}$ were determined from the calibration curve of the standard PS, and were $\simeq 1.1$ for the products labeled "A", $\simeq 1.3$ for "B", and $\simeq 2.1$ (or above) for "C". As shown in the table, PVT-I was highly chlorinated, and the MW distribution was little changed by the chlorination. It was assumed that the electro-chlorination of PVT proceeds with a two-electron transfer, like the anodic halogenation of usual organic substances.[6,8] Thus, a Cl content of 1.14 in the product (Run 2) is equivalent to a 91% current efficiency. During the chlorination of PVT-II, the MW distribution of the product tended to spread, though Cl was introduced into PVT with 0.9 atoms or more per monomer unit (Runs 3—5). The product labeled "C" in the table was not satisfactory as a microresist.[3] A change in the MW distribution was not observed upon decreasing the PVT-II concentration (Runs 6 and 7), but the Cl content in the product was also lowered (<0.1).

The effective chlorination of PVT-II without any change in the MW distribution became feasible upon

TABLE 1. ELECTRO-CHLORINATION OF POLY(VINYLTOLUENE) IN ORGANIC/WATER SUSPENSION SYSTEMS

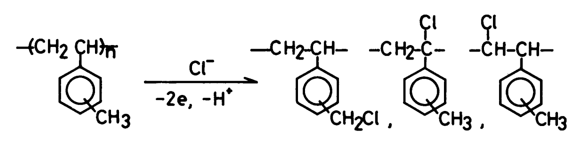
Run$^{a)}$	Organic Solvent$^{b)}$	$W^{c)}$ wt%	Current$^{d)}$ A	Cell voltage$^{e)}$ V	Electric charge F$^{f)}$ (unit-VT mol)$^{-1}$	Cl content in the product atom (unit-VT)$^{-1}$	MW distribution of the product$^{g)}$
1	CH_2Cl_2	3	0.5	4	2.5	1.08	A
2	CH_2Cl_2	5	0.5	4	2.5	1.14	A
3	CH_2Cl_2	5	0.3	3	2.5	0.98	C
4	CH_2Cl_2	5	0.5	3	2.5	0.93	C
5	CH_2Cl_2	5	0.7	5	0.5	0.22	C
6	CH_2Cl_2	1	0.5	4	2.5	<0.1	B
7	CH_2Cl_2	1	0.1	2	2.5	<0.1	B
8	$CHCl_3$	1	0.1	2	2.5	0.29	A
9	C_6H_6	1	0.1	2	2.5	0.47	A
10	C_6H_6	3	0.1	2	2.5	0.89	A
11	C_6H_6	3.3	0.5	3	2.5	0.86	A
12	C_6H_6	1	0.2	2	10.0	1.38	B

a) Runs 1 and 2: PVT-I($\overline{Mn}\simeq 40000$), Runs 3—12: PVT-II($\overline{Mn}\simeq 170000$), b) Organic phase/aqueous phase (12 mol dm^{-3} HCl)=1:1 by volume, c) W is PVT concentration in organic phase, d) Surface area of the anode (Pt): 3.5 cm^2, e) Voltage at the beginning of the electrolysis, f) F denotes 96485 C (2.5 F=2.41×10^5 C), g) Represented qualitatively; A denotes $\overline{Mw}/\overline{Mn}\simeq 1.1$, B$\simeq$1.3, C$\gtrsim$2.1, ($\overline{Mw}/\overline{Mn}$ of the original PVT$\simeq$1.1).

choosing an appropriate solvent for the organic phase. Regarding electrolysis in a $CHCl_3/H_2O$ suspension (Run 8), the MW distribution was little spread, but the Cl content was relatively low. The use of C_6H_6 as a solvent brought about an improvement in the Cl content without broadning of the MW distribution (Runs 9—11). The Cl content increased upon increasing the PVT concentration, but the influence of the current density on the Cl content was rather small. An increase in the electric charge lead to a high Cl content in the product (Run 12). In this case, however, the current efficiency fell to 30% or less, and the MW distribution of the polymer tended to spread. This is probably due to the electrochemical reduction of the product C-PVT at the counter electrode (cathode), where a subtraction of the Cl from the C-PVT and/or a reductive cross-linking of the polymer might occur.

The differences in the results regarding electro-chlorination between PVT-I and PVT-II are probably responsible for the differences in the mean molecular weight and/or the isomer ratio of the starting PVT. On the other hand, solvent properties, such as the donor- and acceptor numbers[9], apparently affected the results of the PVT-II chlorination. It is supposed that the molecular Cl_2 formed by a side reaction is more polarized in CH_2Cl_2 than in C_6H_6. The activated Cl_2 in CH_2Cl_2 would promote the polymer chains to cross-link with each other.

The ^{1}H NMR spectra of the product polymer suggested that chlorination occurred at the methyl group of toluene as well as at the α- and β-positions of the chain (Scheme 2). A variation in the experimental conditions (such as the PVT concentration and the current density) did not seem to affect the chlorinated positions. In the electro-halogenation of low molecular-weight aromatics such as alkylbenzenes[6,10] and alkoxybenzenes,[11–13] nuclear-substituted compounds have been main products. During the present electro-chlorination of PVT, however, nuclear substitution was not detected. The differences in the substitution position might originate from the difference in the solvent that was used. That is, homogeneous organic solutions containing polar solvents were used in previous work for the chlorination of alkyl- or alkoxybenzenes.[6,10–13] However, a suspension of C_6H_6 (or CH_2Cl_2)/H_2O was employed in the present work. These solvent effects, which relate to the details of the reaction mechanism, are now under investigation.



Scheme 2.

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