Solution Decomposition Behavior of Chemically Modified Poly(vinyl chloride)

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Kinetic studies of the evolution of HCl from thermally degrading poly(vinyl chloride)[2] (PVC) have frequently been performed directly on solid polymer samples. While this technique has the advantages of convenience and the prevention of polymer–solvent interactions, it can also lead to difficulties in the interpretation of results, owing to the effects of sample morphology on rates of dehydrochlorination. These effects can be quite pronounced, and various authors have reported, for example, that the dehydrochlorination rate may be either increased[3] or decreased[4] by increasing the particle size; that it is decreased by increasing polymer crystallinity;[5] and that it is influenced in a variety of ways by particle surface area,[4,6] total sample thickness or size,[3,6b,7] and the physical form (powder or film) of the samples.[3b,8] In fact, samples of different particle size obtained from the same bulk polymer by sieving have even been reported to undergo dehydrochlorination at different rates *in solution,*[9] a result which can be attributed to variations in the nature and concentration of labile structural defects (or of catalytic impurities) for particles of different dimensions. On the other hand, the dehydrochlorination behavior of solid PVC is also said to be unaffected by total sample thickness or size under certain experimental conditions,[3b,7c,10] and it is now clear that many of the kinetic phenomena observed with the neat polymer can be ascribed to morphological effects on rates of HCl diffusion and on the extent to which the dehydrochlorination is catalyzed by entrapped HCl.[2c,d,3,4,6–8a,9] However, the quantitative influence of such factors remains difficult to assess,[11] and the problem is complicated by kinetic effects produced by the other experimental variables (e.g., flow rate of carrier gas) which can alter the concentration of HCl in and around the polymer matrix.

Recently we reported rates of thermal dehydrochlorination under argon for several solid samples of chemically modified PVC that had been prepared by pretreatment of the polymer with a variety of organotins.[12] In that work precautions were taken to minimize the kinetic effects of morphology or, at least, to keep them constant from sample to sample; i.e., rate constants were shown to be independent of total sample weight and the rate of inert-gas sweeping.[12a] Particle size was controlled qualitatively rather than quantitatively, but the existence of an inverse correlation between dehydrochlorination rate and sulfur content (for polymers pretreated with an organotin mercaptide) indicated that the observed rate differences were due to differences in chemical constitution rather than polymer morphology.[12a] Nevertheless, in view of the considerations noted above, we felt it would be desirable to confirm this conclusion by measuring the dehydrochlorination rates of the modified polymers under conditions where morphological factors would be excluded in their entirety. A brief investigation of this type is described in the present paper.

Results and Discussion

Chemically modified PVC's were prepared as usual by allowing the virgin polymer to react with mixtures of di(*n*-butyl)tin dichloride and the corresponding dilaurate, bis(*n*-dodecyl mercaptide), or β-mercaptopropionate.[12] The reactions were carried out under nitrogen in *o*-dichlorobenzene solution, and the product polymers were purified by methanol precipitation and extraction according to our standard procedure.[12a] The polymers were then subjected to infrared and/or elemental analysis, and their rates of dehydrochlorination were determined under argon in *o*-dichlorobenzene at 158.4 °C. Samples of random particle size were used for the solution decompositions in order to avoid kinetic effects of the type observed by Onozuka and Asahina[9] (see above). Data for these experiments are presented in Table I, together with information pertaining to similar polymers that were decomposed as powders at 160.5 °C. Columns 1–3 of the table refer to pretreatment conditions; the remaining columns list polymer properties. In view of the use of nearly equivalent preparative conditions and the similarities revealed by the analytical results of columns 4–6, the modified polymers that were decomposed in solution are considered to be structurally comparable to the polymers employed for parallel solid-phase decomposition runs.

The solution decompositions were found to be much slower than those of the solid samples, and the slowest solution rates were difficult to determine accurately due to the necessity of

Table I
Preparation, Analysis, and Decomposition of Chemically Modified PVC

Organotin[b]	React temp,[c] °C	React time, h	Sulfur, %	Tin, ppm	Abs. ratio[d]	k,[a] mol HCl (g PVC)$^{-1}$ h^{-1} × 10^6	
						o-$Cl_2C_6H_4$[e]	Solid[f]
					1.1 ± 0.1[g,h]	2.5 ± 0.2[i]	10.1 ± 0.5[j]
	78	0.2			0.7[h]	2.2[k]	7.8 ± 0.8[l]
n-Bu_2SnL_2[m]	185	75		<4[h,n]	8.1[h]		5.6
				6[h]	7.2[h]		5.5
				76[h]	7.7[h]		3.2
n-Bu_2SnL_2	182	75		6[o]	7.8	1.1 ± 0.1[l]	
n-$Bu_2Sn(DM)_2$	185	75	1.05[h]	17[h]			4.0
n-$Bu_2Sn(DM)_2$[p]	180	74	0.55	<5[n,o]		0.6 ± 0.0[l]	
				<5[n,o]		0.4	
n-$Bu_2Sn(BMP)$	182	75	0.40[h]	45[h]	10.7[h]		0.88
n-$Bu_2Sn(BMP)$	185	75	0.52	15[o]	10.2	0.3 ± 0.1[l]	

[a] Measured under Ar. [b] Reactions were carried out under N_2 in *o*-$Cl_2C_6H_4$ (100 ml/g PVC) containing the organotin (3.1 × 10^{-3} mol/g PVC) and *n*-Bu_2SnCl_2 (2.2 × 10^{-3} mol/g PVC); MeOH extraction time ≃ 24 h. L = *n*-$C_{11}H_{23}CO_2$, DM = *n*-$C_{12}H_{25}S$, BMP = $-SCH_2CH_2CO_2$. [c] ±5 °C. [d] (Ester carbonyl absorbance at ~1725 cm^{-1})/(absorbance at 2550 cm^{-1}). [e] Solution temp = 158.4 ± 0.3 °C; PVC concn = 9.39 ± 0.01 g/L unless noted otherwise. [f] Bath temp = 160.5 ± 0.2 °C; PVC = 0.375 ± 0.002 g; data from ref 12c. [g] Mean deviation for five samples. [h] Taken from ref 12c. [i] Mean deviation for four runs. Measurements with different amounts of polymer indicated that the dehydrochlorination rate was first order in PVC in the concentration range of interest. [j] Mean deviation for twelve runs. [k] PVC concn = 7.20 g/L. [l] Mean deviation for two runs. [m] Experiment performed in triplicate. [n] No Sn detected. [o] Estimated by x-ray fluorescence. [p] Experiment performed in duplicate.

applying a rather large correction for the solvent blank (see Experimental Section). Nevertheless, column 7 of Table I clearly shows that, in solution, all of the modified polymers were much more stable than virgin PVC (line 1) or PVC which had been subjected to the dissolution–precipitation–extraction sequence used for the chemical modification treatments (line 2). Further, it will be noted that the order of the average stabilities found for the modified polymers in solution is identical to the order observed for the samples that were decomposed in powder form (column 8). Thus, generally speaking, the solution decomposition data provide strong support for our earlier conclusions derived from powder decomposition work.[12] However, the present results do not rule out the possibility that morphological effects were responsible for some of the minor rate differences observed with the solid materials. For example, a comparison of the first two *k* values in column 7 with the first two in column 8 suggests that the slightly improved stability observed for the solid samples of reprecipitated virgin PVC may have been primarily due to changes in polymer morphology.

Elemental analyses reported here and in earlier papers[12] indicate that the modified polymers of Table I contained only about 2.5–11 stabilizer ligands per 1000 atoms of carbon. These low values are, of course, consistent with the selective destruction of defect sites by ligand substitution, as proposed in the stabilization theory of Frye and Horst.[13] However, for reasons discussed elsewhere,[12a] we prefer not to regard these values as a measure of the number of unusually labile halogens originally present in virgin polymer.

Experimental Section

Materials. The starting PVC was Geon 103EP, an unstabilized commercial product (Goodrich) that had been used in some of our earlier work.[12c] Burdick and Jackson "distilled in glass" *o*-dichlorobenzene was employed as the solvent for solution decomposition kinetics; it contained traces of the corresponding para isomer and monochlorobenzene but had no other impurities detectable by GC-mass spectrometry (analysis by Dr. D. J. Freed). All other materials used in this study were described in previous papers.[12]

Chemical Modification Experiments. Procedural details are given elsewhere for the chemical modification reactions[12a] and for infrared analysis of the products obtained.[12c] The reactions with the sulfur-containing organotins produced small amounts of a black precipitate[12a] which was removed by filtration or decantation prior to precipitation of the polymer with methanol. The x-ray fluorescence method used for some of the tin analyses (see Table I) was developed and performed by Miss S. M. Vincent. All other elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Dehydrochlorination Kinetics. Solution dehydrochlorinations were carried out in an all-glass apparatus similar to that used with powder samples[3b,12] but modified by inclusion of a short water-cooled reflux condenser, a coarse fritted-glass bubbler that permitted efficient sweeping of solutions with the argon carrier gas, and a thermocouple well that allowed solution temperature to be monitored directly. Solutions were prepared in situ by heating mixtures of polymer and solvent while agitating by argon bubbling; all solutions were continuously swept with argon after preparation and were allowed to equilibrate under the reaction conditions for at least 15 min prior to the start of kinetic runs. Evolution of HCl was followed by continuous titration with 0.0100 N aqueous sodium hydroxide using a Sargent Recording pH Stat (Model S-30240); in other respects the kinetics procedure was essentially equivalent to the method employed with solid polymer.[12] Control experiments showed that the solution dehydrochlorination rates were independent of argon flow rate under the conditions chosen for use. Shapes of kinetic curves were generally similar to those obtained with solid PVC (initial autoacceleration followed by linearity), and most of the reactions were allowed to run overnight to ensure that linearity was achieved. Rate constants were calculated from the linear portions of the curves in the manner previously described.[12a,b] Blank runs indicated an apparent evolution of "acid" (an instrumental artifact?) from pure solvent alone (40 ml) at the rate of 0.1×10^{-6} mol/h, and all of the solution decomposition *k*'s recorded in Table I have therefore been corrected accordingly. Thus, for experiments with 0.375 g of polymer in 40 ml of solution (corresponding to 9.38 g/L), the *k*'s calculated from overall acid evolution rates were adjusted by subtracting a blank correction of 0.3×10^{-6} mol HCl (g PVC)$^{-1}$ h^{-1}.

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