Carbon-13 Labeling Studies of Volatile Pyrolyzate Formation from Poly(vinyl Chloride)

INTRODUCTION

The first step in inert atmosphere PVC thermal degradation is dehydrochlorination. Loss of HCl leaves as a residue a conjugated polyene structure that can undergo further pyrolysis to yield a vast array of aliphatic and aromatic hydrocarbon products. Deuterium labeling experiments using pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) have shown that benzene[1-3] and naphthalene[2,3] form from PVC via intramolecular cyclization of the polyene chain. Specific hydrogen transfer reactions were found to be important in the formation of mixed "aromatic–aliphatic" pyrolyzates from PVC (e.g., toluene, methylnaphthalene, styrene, and indene).[3] A key result of these deuterium labeling studies was that crosslinking (intermolecular C—C bond formation) reactions are apparently not very important in the formation of volatile aromatic pyrolyzates from PVC.[3] This could not be proven definitively in these earlier studies, however, since the carbon atoms were not labeled.

In this note we describe the preparation and use of ^{13}C-labeled PVC as a tracer compound to study volatile pyrolyzate formation in PVC. Py–GC–MS has been used to measure the ^{12}C/^{13}C distributions in experiments with intimately mixed ^{12}C$_2$–PVC and ^{13}C$_2$–PVC (without additives). We find that very little, if any, mixing of ^{12}C and ^{13}C occurs in either the aromatic or aliphatic pyrolyzates. This is consistent with recent isotopic labeling experiments conducted by Starnes et al.[4]; it is also consistent with our detailed deuterium labeling studies.[3] We believe that the results of these ^{13}C-labeling experiments give considerable new insight into basic pyrolysis mechanisms in PVC.

EXPERIMENTAL

^{13}C$_2$–vinyl chloride monomer (VCM) was purchased from Cambridge Isotope Laboratories (Cambridge, MA). Analysis by GC–MS showed a ^{13}C enrichment of ~99.5 atom %. GC–MS also revealed several low-level impurities in the monomer–chloroacetylene, dichloroacetylene, dichloroethene, ethanol, and fluorotrichloromethane.

The ^{13}C$_2$–VCM was polymerized in a 5 cm^3 sealed Pyrex tube. The tube was charged with 0.40 g ^{13}C$_2$–VCM, 2.0 g methanol, and 0.00124 g sec-butylperoxydicarbonate (SBP). The polymerization tube was flushed with nitrogen, the SBP/methanol solution was added, and the tube was cooled in dry ice. The ^{13}C$_2$–VCM was added by injecting the gas under the surface of the cold liquid. Using a Pyrex capillary, nitrogen was bubbled slowly through the mixture. After 1 min the tube was sealed with a torch. The nitrogen purge was continued until the flame collapsed the capillary.

The sealed tube was tumbled for 16 h at 50°C. The tan, waxy product was dissolved in tetrahydrofuran and precipitated with methanol. The yield of polymer was 59 mg (15%). A control sample was prepared under the same conditions using ^{12}C$_2$–VCM; the yield of polymer (a white powder) was 62%.

A CDS Model 100 Pyroprobe was used for pyrolysis. Pyrolyses were conducted in dry helium at a flow rate of ~30 cm^3/min. Some experiments were conducted with the platinum ribbon probe (pyrolysis at 600°C for 20 s).[3] Polymer samples were deposited on the ribbon via syringe from tetrahydrofuran solution. Other experiments were conducted with the platinum coil probe (pyrolysis at 550°C for 20 s).[2] Solid polymer samples were placed in Pyrex pyrolysis tubes (with glass wool to hold the polymer in place).

The pyrolyzates were analyzed by GC–MS. The GC–MS system consisted of a Varian 3700 gas chromatograph, a Finnigan MAT 311A mass spectrometer, and a Finnigan Incos 2400 data system. Lower boiling pyrolyzates (up to C$_6$) were separated on a 2 m × 2 mm ID glass Porapak S column, programmed from 50°C to 200°C at 8 deg/min with no hold on injection. Higher boiling pyrolyzates (greater than C$_6$) were separated on a 2 m × 2 mm ID glass 3% Dexsil 300 on 100/120 mesh Supelcoport column, programmed from 50°C to 250°C at 8 deg/min with a 2-min hold on injection.

The Py–GC–MS runs were made in electron impact mode (38 eV). For the hydrocarbons of interest, the molecular ion region showed only M$^{+\cdot}$ (base peak) and (M—H)$^+$ ions. Control experi-

ments were run in which 40 μg $^{12}C_2$–PVC was applied to one side of the ribbon probe and 92 μg $^{13}C_2$–PVC was applied to the other side of the ribbon. Py–GC–MS data for these runs were used to determine correction factors for (1) the abundances of the $(M—H)^+$ ions, (2) the natural abundance of ^{13}C in the $^{12}C_2$–PVC sample, and (3) the small abundance of ^{12}C in the $^{13}C_2$–PVC sample.

The $^{13}C_2$–PVC showed higher than normal levels of chlorine-containing pyrolyzates (e.g., chlorobenzene, dichlorobenzene, and chlorotoluene). These chlorine compounds were evidently formed from the known impurities that had copolymerized with the vinyl chloride. The presence of these chlorine-containing pyrolyzates did not interfere with the interpretation of results from the pyrolysis experiments.

Two types of pyrolysis experiments were carried out. For experiments using the ribbon probe,[3] a solution of $^{12}C_2$–PVC and $^{13}C_2$–PVC was prepared in tetrahydrofuran. The polymer (54 μg $^{13}C_2$–PVC plus 33 μg $^{12}C_2$–PVC) was deposited on the ribbon by syringe, and the solvent was allowed to evaporate with gentle heating at 100°C. An excess of $^{13}C_2$–PVC was used, since the hydrocarbon pyrolyzate yields were lower for this polymer. Isotopic abundances for several pyrolyzates were determined from Py–GC–MS data, and the results are given in Table I.

For experiments using the coil probe,[2] a solid coprecipitate of $^{12}C_2$–PVC and $^{13}C_2$–PVC was prepared. Equal weights of the two polymers (22 mg each) were dissolved in 1 cm³ tetrahydrofuran. The polymers were then coprecipitated with 2 cm³ methanol. To conserve material, the mixed solvent was simply evaporated off under a stream of nitrogen. The dried coprecipitate was placed as a solid (1.0 ± 0.1 mg) in the Pyrex pyrolysis tubes and subsequently pyrolyzed. Isotopic abundances for several pyrolyzates are given in Table I.

RESULTS AND DISCUSSION

Very little, if any, mixing of ^{12}C and ^{13}C isotopes was detected in any of the pyrolyzates listed in Table I. This was true for experiments with the ribbon probe (87 μg polymer) as well as the coil probe (1.0 mg polymer). A few of the experiments indicate that there may be limited mixing of ^{12}C and ^{13}C in the pyrolyzates (up to ~6%), but this should be considered an upper limit to the amount of mixing that may have occurred. It is difficult to accurately measure isotopic species that make up less than 1–2% of the total, due to background ions, chromatographic interferences, and proton losses from molecular ions. Nevertheless, it is clear that any mixing of ^{12}C and ^{13}C isotopes in these experiments was very minor. The results in Table I are consistent with recent ^{13}C labeling results of Starnes et al., who found little $^{12}C/^{13}C$ mixing in benzene, toluene, and naphthalene pyrolyzates from PVC.[4]

A possible explanation for the lack of mixing of ^{12}C and ^{13}C isotopes in the volatile pyrolyzates would be that the $^{12}C_2$–PVC/$^{13}C_2$–PVC samples were not well mixed prior to pyrolysis. Our earlier experience with mixed PVC/perdeutero-PVC,[2,3] however, indicates that either the syringe deposition or coprecipitation technique results in intimate mixing of the PVC chains. We thus believe that the $^{13}C_2$–PVC/$^{13}C_2$–PVC samples were well mixed in these experiments. The $^{13}C_2$–PVC was a lightly colored, low molecular weight material, but it dissolved well in tetrahydrofuran.

We conclude that for PVC without additives, the aromatic and aliphatic pyrolyzates form exclusively (or almost exclusively) from noncrosslinked segments of the decomposing PVC chains. This does not mean that there is no crosslinking (intermolecular C—C bond formation), but it does show that crosslinked portions of the decomposing polymer do not give rise to volatile pyrolyzates. This conclusion was tentatively stated in our earlier study dealing with deuterium-labeled PVC.[3] Hydrogen transfer reactions were shown to be important in volatile hydrocarbon pyrolyzate formation, but the results of our deuterium labeling studies could be adequately explained without invoking crosslinking mechanisms.

The above statements are true for both aromatic and aliphatic pyrolyzates. Intermolecular hydrogen transfer reactions are in general more important in forming aliphatic pyrolyzates than in forming the aromatics.[3] In summary we can state that volatile pyrolyzate formation from PVC is intermolecular with respect to hydrogen, but intramolecular with respect to carbon.

TABLE I
Isotopic Distributions of Selected $^{12}C_2$–PVC/$^{13}C_2$–PVC Pyrolyzates

Isotopic species		Percent abundance[a]		Isotopic species		Percent abundance[a]	
MW	^{13}C	Ribbon[c]	Coil[c]	MW	^{13}C	Ribbon[b]	Coil[c]
Ethylene				*Benzene*			
28	0	46	50	78	0	53	60
29	1	0	0	79	1	0.6	0.2
30	2	54	50	80	2	0	0
				81	3	0.1	0
1,3-Butadiene				82	4	0.5	0
54	0	58	63	83	5	0.6	0.2
55	1	0	0	84	6	45	40
56	2	0	0				
57	3	0	0	*Toluene*			
58	4	42	37	92	0	51	62
				93	1	0.6	0.4
1-Butene				94	2	0.9	0
56	0	87	77	95	3	1.0	0.1
57	1	0.3	0	96	4	0	0
58	2	0	0	97	5	0.6	0.6
59	3	0	0.8	98	6	0.8	1.4
60	4	13	22	99	7	45	36
Indene				*1- and 2-Methylnaphthalene*			
116	0	50	58	142	0	48	63
117	1	0.8	1.7	143	1	1.7	2.1
118	2	0	0.2	144	2	0	0
119	3	0	0.9	145	3	2.0	0
120	4	0.6	0.8	146	4	1.0	0
121	5	0	0.7	147	5	0.5	0
122	6	0.1	0.5	148	6	0.1	0
123	7	0	0.6	149	7	0	0
124	8	0	0.8	150	8	0.3	0.2
125	9	49	36	151	9	0.2	0.6
				152	10	0	0.8
Naphthalene				153	11	46	33
128	0	49	64				
129	1	0.9	2.1				
130	2	0	1.1				
131	3	0	0				
132	4	0	0				
133	5	0.4	0				
134	6	0.2	0.5				
135	7	0.3	0.5				
136	8	0.1	0.2				
137	9	0.1	0.3				
138	10	49	31				

[a] Determined from Py–GC–MS (38 eV EI) molecular ion intensities; average of triplicate runs. Corrections have been made for (1) the intensities of the (M—H)$^+$ fragment ions, (2) the natural abundance of ^{13}C in the $^{12}C_2$–PVC sample, and (3) the small abundance ($\sim$0.5%) of ^{12}C in the $^{13}C_2$–PVC sample.

[b] Coprecipitate of $^{12}C_2$–PVC (33 μg) and $^{13}C_2$–PVC (54 μg) on ribbon probe.

[c] Coprecipitate of $^{12}C_2$–PVC (0.5 mg) and $^{13}C_2$–PVC (0.5 mg) in coil probe.

References

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