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Investigation of Chlorinated Poly(Propylene Oxide) and Polyepichlorohydrin by Direct Pyrolysis Mass Spectrometry

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The thermal degradation of chlorinated poly(propylene oxide) and polyepichlorohydrin samples were studied with the use of direct pyrolysis mass spectrometry. The data indicated that chlorine atoms were gathered on some repeating units leaving the rest intact in case of chlorinated poly(propylene oxide). On the other hand, a more homogenous structure with a uniform thermal behavior was detected for chlorinated polyepichlorohydrin.

Keywords chlorinated poly(propylene oxide), chlorinated polyepichlorohydrin, direct pyrolysis mass spectrometry, thermal degradation

Introduction

Glycidyl azide polymer, GAP, is one of the most widely used energetic polymers that decompose very rapidly at low temperatures and produce fuel-rich decomposition products (1–3). It is proposed for use as a binder in solid rocket motors, and its thermal decomposition has been studied extensively. In general, GAP is synthesized by substitution of chlorine atoms of polyepichlorohydrin, PECH, with azide groups of sodium azide. Even more energetic polymers may be synthesized by increasing the number of azide groups per repeating units. Recently, the azidization of chlorinated poly(propylene oxide), PPO, and polyepichlorohydrin, (PECH), were achieved and modified glycidyl azide polymers were synthesized with up to 4.2 azide groups per repeating units of PPO and PECH (4).

It is known that in the chlorination of alkanes more than one monochloroalkane can be formed. Thus, chlorination of PPO and PECH was expected to yield a mixture of polymer chains with various distributions of chlorine atoms in each repeating unit. Though, it has significant importance, this distribution could not be determined with the use of classical spectrometric techniques. One possible solution is the application of direct pyrolysis mass spectrometry, DPMS, technique for elucidating the distribution of chlorine atoms in each repeating unit of PPO and PECH. Thermal degradation and structural analysis of polymers have been extensively studied with the application of pyrolysis mass spectrometry

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techniques (5, 6). However, the lack of a standard library to facilitate the data interpretation and the complexity of the pyrolysis mass spectra limit the routine applications.

There have been extensive studies on the characterization of oxidative and thermal degradation pathways and the products of poly(propylene oxides), PPO, because of the importance in polyurethane elastomers and foams that undergo rapid oxidative degradation at elevated temperatures (7–9). It has been determined that the main thermal decomposition mechanism of PPO involves homolytic chain scission at the C–O bonds, followed by hydrogen transfer reactions. Other series of thermal degradation products, though less abundant, arise from cleavage at β-C and are also stabilized by H-transfer reactions. Thus, it has been concluded that poly(propylene oxide) degrade via random cleavage mechanism, the labile C–O bond scissions being preferred. It has also been determined that thermal decomposition mechanism of PPO is also valid for the thermal degradation of PECH. However, for PECH, significant reductions in the relative yields of oligomers and increase in products due to elimination of side groups and loss of Cl are noted (10–13).

In this study, we applied direct pyrolysis mass spectrometry not only to investigate thermal degradation behaviour, but also to determine structural characteristics of chlorinated PPO and PECH samples prepared in our laboratories.

Experimental

Propylene oxide was a product of Merck AG. It was refluxed over CaH_2 for several days before fractionation. Purification of the monomer and poly(propylene oxide), (PPO) preparation was discussed in the literatures (4). Polyepichlorohydrin (PECH) was supplied from 3M Company and used without further purification. Chlorination of PPO and PECH were discussed in our previous publication in details (4). Basically, Cl_2 gas was bubbled in PPO/CCl_4 and $PECH/CCl_4$ solutions for several days at 60°C. The extent of chlorination was determined both from stoichiometry and volumetric determination of chloride anions formed by the combustion of the samples according to Mohr's method as 0.8, 3.1 and 3.8 chlorine atoms per repeating unit of PPO (denoted as Cl-PPO-0.8, Cl-PPO-3.2 and Cl-PPO-3.8) and 4.3 chlorine atoms per repeating unit of PECH (denoted as Cl-PECH-4.3).

The direct insertion probe mass spectrometry system used for the thermal analyses consists of a 5973 HP quadrupole mass spectrometry with a mass range of 10–800 amu coupled to a SIS direct insertion probe pyrolysis system. The maximum temperature that can be attained is 445°C. Thermal decomposition of the samples was studied applying two heating rates namely, 10°C/min and 900°C/min. Mass spectra were acquired at a rate of 2 scans/s using 70 eV electrons. Experiments were repeated decreasing ionization energy to 19 eV to minimize dissociation of the thermal decomposition products in the ion source of the mass spectrometry system. 0.01 mg samples were pyrolyzed in the flared glass sample vials.

Results and Discussions

The pyrolysis of chlorinated PPO samples indicated that thermal decomposition of these polymers occurs over a broad temperature range. The total ion current (TIC) curves, the variation of total ion yield as a function of temperature, showed several peaks that can directly be associated with the presence of chain segments with different thermal stabilities and thus structures. The pyrolysis mass spectra of chlorine substituted PPO samples were complex and indicated that the polymer samples did not have uniform structure. However, with the use of isotopic abundances of Cl-35 and Cl-37 isotopes, interpretation of the products involving chlorine atoms was rather simple. The pyrolysis mass spectra of PPO, Cl-PPO-0.8, and Cl-PPO-3.8 are shown in Figure 1(a), (b), and (c), and the related data are summarized in Table 1. The data related to PPO are also included in the table for comparison. Characteristic peaks due to the monomer and the oligomers of PO were present in the pyrolysis mass spectra of all the chlorinated polymers. Thus, it is clear that even for the Cl-PPO-3.8, chlorination of each repeating unit could not be achieved.

For Cl-PPO-0.8, the PO monomer peak at m/z = 59 Da was the base peak, as in the case of PPO (13). However, a significant decrease in the relative intensities of oligomer peaks was detected. Cluster peaks that can directly be attributed to $CHCl_2$ and to CCl_3 were present. Although the contribution of PO dimer to CCl_3 peak at m/z = 117 Da was quite significant, the presence of peaks at m/z = 119, 121 and 123 Da with intensity ratios about 27/9/1 confirms the evolution of CCl_3. Furthermore, a cluster of peaks that can be related to $C_3H_xCl_{6-x}O$ where x = 5, 3, 2, 1 or 0 were identified. Thus, it may be concluded that chlorine atoms were gathered on some repeating units, leaving the rest of the units intact. It can further be proposed that as a result of chlorination,

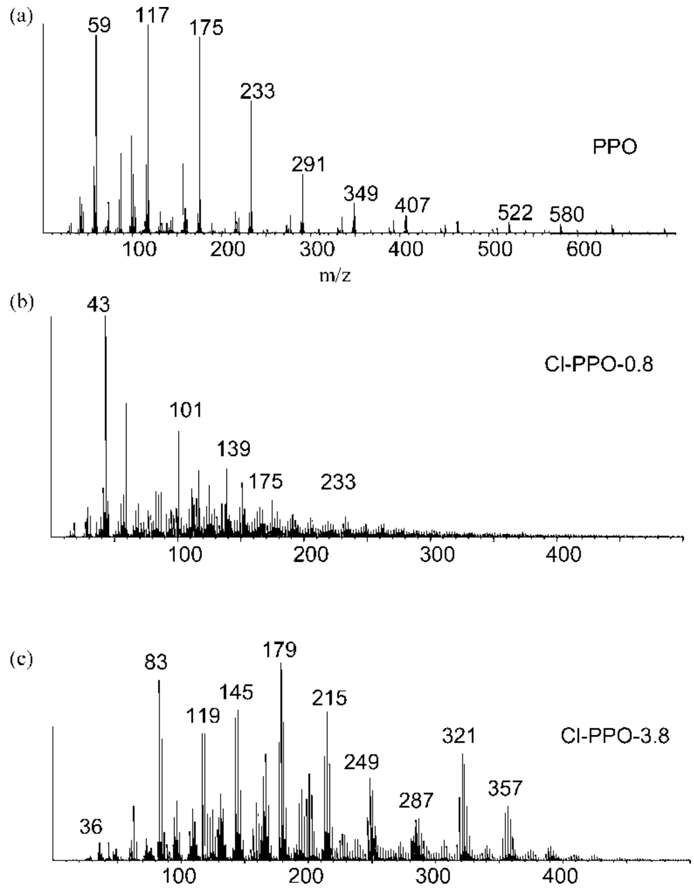

Figure 1. The pyrolysis mass spectra of (a) PPO, (b) Cl-PPO-0.8, and (c) Cl-PPO-3.8.

Table 1

Relative intensities of characteristic product peaks recorded during the pyrolysis of PPO, Cl-PPO-0.8, and Cl-PPO-3.8

m/z	PPO	Cl-PPO-0.8	Cl-PPO-3.8	Assignments
28	10	18		CH_2OH
36		3	8	HCl
43	34	92	10	$CH_2CH{=}O$
59	100	100	2	$CH_2CH(CH_3)OH$, $CH_3CH(CH_3)O$
65		3–4	24	CClO
83	5	23	82	$CHCl_2$
85	22	40	56	$CH_2CH(CH_3)OC_2H_3$, $CHCl_2$
87	52	41	13	$C_2H_5OCH_2CH(CH_3)$
95	4	14	21	C_2HCl_2
101	54	75		$CH_2CH(CH_3)OC_2H_3O$
107	2	6	17	C_3HCl_2
109	3	11	24	$C_3H_3Cl_2$, C_3HCl_2
117	98	49	71	$(CH_2CH(CH_3)O)_2H$, CCl_3
119		25	73	CCl_3
125	2	31	22	$C_3H_3Cl_2O$
133	5	6	22	C_2Cl_3,
143	11	6	57	$(CH_2CH(CH_3)O)_2C_2H_3$, $C_3H_2Cl_3$
145	17	9	61	$C_2H_5\ (OCH_2CH(CH_3))_2$ $C_3H_2Cl_3$
159	22	9	23	$(CH_2CH(CH_3)O)_2C_2H_3O$, $C_3H_2Cl_3O$
164			21	C_2Cl_4
165			40	$C_3H_4Cl_3O$, C_2HCl_4
175	85	18	2	$(CH_2CH(CH_3)O)_3H$
177	3	8	63	C_3HCl_4
179	2	11	100	C_3HCl_4, $C_3H_3Cl_4$
193	3	12	27	C_3HCl_4O
201	4	6	44	$(CH_2CH(CH_3)O)_3C_2H_3$
203	7	7	33	$C_2H_5\ (OCH_2CH(CH_3))_3$
213	1	4	42	$C_3H_2Cl_5$
215	5	4	59	$(CH_2CH(CH_3)O)_3C_3H_5$ $C_3H_2Cl_5$
227		5	15	C_3Cl_5O
247		6	18	$(CH_2CH(CH_3)O)_4CH_3$, C_3HCl_6, $C_6H_3Cl_4O_2$
249		5	38	$C_6H_5Cl_4O_2$
319		1	43	$(C_3H_3Cl_3O)_2H$,
321		2	74	$(C_3H_3Cl_3O)_2H$

long chains of PO repeating units that would produce high yield of oligomers during thermal degradation were disappeared noticeably.

The PPO monomer peak diminished significantly for Cl-PPO-3.2 and nearly disappeared for Cl-PPO-3.8. For Cl-PPO-3.2, the base peak was at $m/z = 83$ Da due to $CHCl_2$ and for Cl-PPO-3.8, the base peak was at $m/z = 179$ Da due to C_3HCl_4. For these samples, the peaks due to $C_3H_xCl_{6\text{-}x}O$ where $x = 1$, 2 or 3 were enhanced. It is clear that the relative intensities of the peaks attributed to greater number of chloro substituted repeating units increased in the order Cl-PPO-0.8 $<$ Cl-PPO-3.2 $<$ Cl-PPO-3.8 as expected. Yet, the relative intensities of dimer and oligomer peaks associated with four or more chlorine substituted repeating units were significantly low. It is known that as the size of the molecule increases the relative intensity of the ion decreases. Thus, the lack of intense oligomer peaks may be as a result of further dissociation during the ionization process in the mass spectrometer. It is clear that Cl atoms were not randomly distributed over the C atoms but they were preferentially accumulated on some repeating units. Even for the Cl-PPO-0.8, weak isotopic peaks due to C_3Cl_5O at $m/z = 227, 229, 231, 233, 235, 237$ were detected indicating that chlorine atoms were gathered on some repeating units, leaving the rest of the units intact. This tendency can be explained as the reactivity of a repeating unit (or carbon atom) increases as the number of Cl atoms on that repeating unit increases and is well known in the chlorination of methane.

When the polymer sample prepared by chlorination of PECH was analyzed, a more uniform distribution was noted. The total ion current curve of Cl-PECH-4.3 shows a

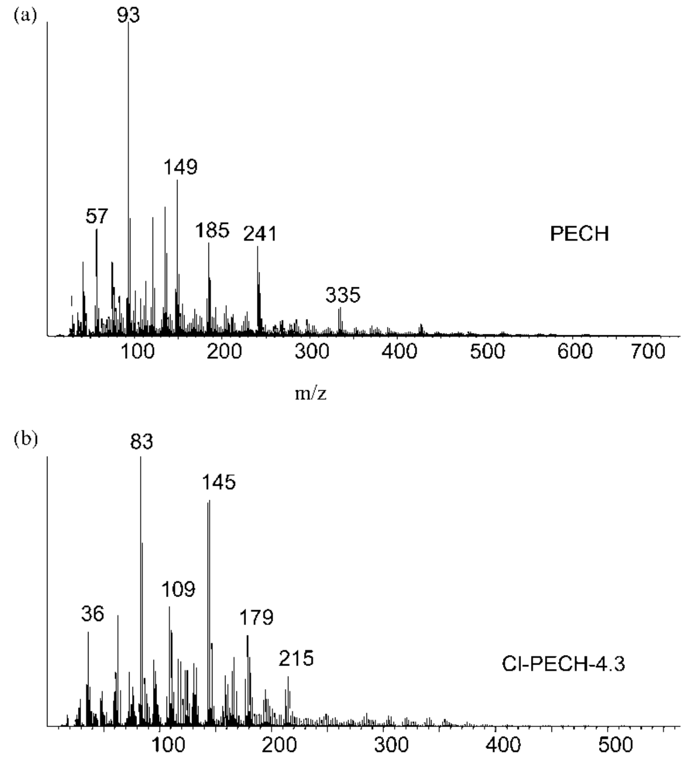

Figure 2. The pyrolysis mass spectra of (a) PECH, and (b) Cl-PECH-4.2.

single peak with a maximum at 280°C indicating that the thermal stability of PECH decreased significantly upon chlorination. In Figure 2, the pyrolysis mass spectrum recorded at 280°C for Cl-PECH-4.3 is shown. That of PECH is also included for comparison. In Table 2, the related mass spectral data are summarized. Note that, in the case of PECH, two degradation stages were noted. The presence of more than one peak or shoulders in the TIC curve indicates a multi-step degradation mechanism or/and presence of blocks with different thermal stabilities. Polydispersity may also be another cause. It has been determined that, during the chlorination of PECH, a large excess of initially present double bonds was chlorinated and some degradation has occurred. The number average molecular weight decreased from 6700 to 5900 of the polymer measured by end group analysis (4). Both of these would cause a decrease in thermal stability besides the changes in the structure due to chlorination.

Table 2
Relative intensities of characteristic product peaks recorded during the pyrolysis of PECH and Cl-PECH-4.2

m/z	PECH at 370°C	PECH at 420°C	Cl-PECH at 280°C	Assignments
36	8	11	34	HCl
41	25	52		C_2HO
43	20	29		C_2H_3O
49	3	6	13	CH_2Cl
57	32	50	3	C_3H_5O
63		10	40	CClO
83	8	17	100	$CHCl_2$
91	9	13		$CHC(CH_2Cl)OH$
93	100	100	1	$CH_2CH(CH_2Cl)OH$
95		38	24	C_2HCl_2
107	9	10	11	$CH_2CH(CH_2Cl)OCH_3$, C_3HCl_2
109		4	44	C_3HCl_2
117			26	CCl_3
125			21	$C_3H_3Cl_2O$
131			23	C_2Cl_3
143			81	$C_3H_2Cl_3$
149	38	28	7	$CH_2CH(CH_2Cl)OC_3H_5O$
159			19	$C_3H_2Cl_3O$
165			20	C_2HCl_4
177			17	C_3HCl_4
179			32	C_3HCl_4
185	26	16	4	$(CH_2CH(CH_2Cl)O)_2H$, C_3HCl_4
195			14	C_3HCl_4O
213	4	3	14	$C_2H_5\ (OCH_2CH(CH_2Cl))_2$, $C_3H_2Cl_5$
241	26	12		$(CH_2CH(CH_2Cl)O)_2C_3H_5O$

Analysis of pyrolysis mass spectra indicated that for this sample, the monomer and oligomer peaks characteristic to PECH almost totally disappeared. It is clear that chlorination of each repeating unit has taken place. As each repeat unit of PECH already involves a chlorine atom, reactivity towards chlorination must be identical and the chlorination of each group could occur more uniformly. On the other hand, although products involving four or five chlorine atoms were detected the relative intensity of the cluster peaks starting at $m/z = 117\,Da$ due to the isotopic peaks of CCl_3 were noticeably weak. Although, the average number of Cl atoms per repeat unit is slightly higher for Cl-PECH-4.3, cluster peaks due to hexachloro substituted repeat units were not detectable and those due to penta substituted repeating units were quite diminished compared to those detected for Cl-PPO-3.8. On the other hand, HCl evolution was quite significant compared to all chlorinated PPO samples and starting material PECH. Thus, it is clear that during the ionization processes inside the mass spectrometer, evolution of HCl from the thermal degradation products took place. This would cause a decrease in the number of substituted chlorine atoms detected.

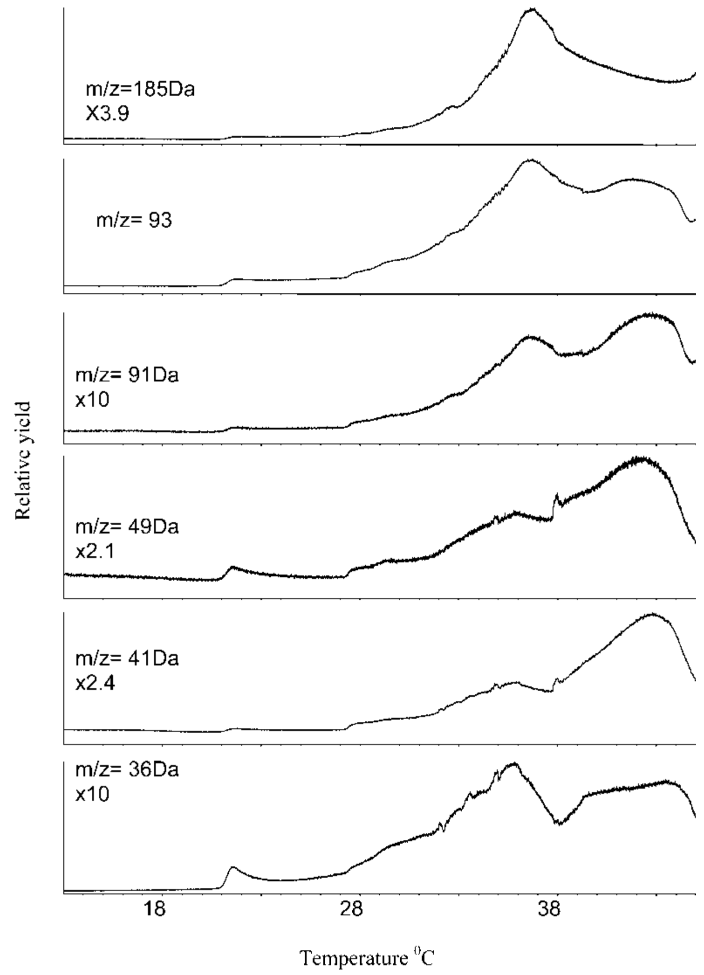

Figure 3. Evolution profiles of selected degradation products of PECH.

To get a better understanding, the evolution profiles of intense and characteristic products of Cl-PECH-4.3 were studied and compared with those detected for PECH in Figure 3, single ion pyrograms, the evolution of a product as a function of temperature, of HCl at m/z = 36 Da, CH═CO at m/z = 41 Da, CH_2Cl at m/z = 49 Da, CH═C(CH_2-Cl)OH at m/z = 91 Da, $CH_2CH(CH_2Cl)OH$ at m/z = 93 Da, and $(CH_2CH(CH_2Cl)O)_2H$ at m/z = 185 Da detected during the pyrolysis of PECH are shown. Note that, the evolution of products involving double bonds and the loss of CH_2Cl group were more pronounced at higher temperatures. It is known that when the main chain is stabilized by double bonds, loss of side chains are enhanced. Thus, it may be concluded that the trends in the TIC curve, the presence of two peaks were mainly due to the presence of blocks involving unsaturation. In Figure 4, the evolution profiles of HCl at m/z = 36 Da, $CH_2CH(CH_2Cl)OH$ at m/z = 93 Da, $CHCl_2$ at m/z = 83 Da, CCl_3 at m/z = 117 Da, $C_3H_2Cl_3$ at m/z = 143 Da and C_3HCl_4 at m/z = 213 Da are shown. To our surprise, all the products showed identical single ion programs, unlike PPO and PECH,

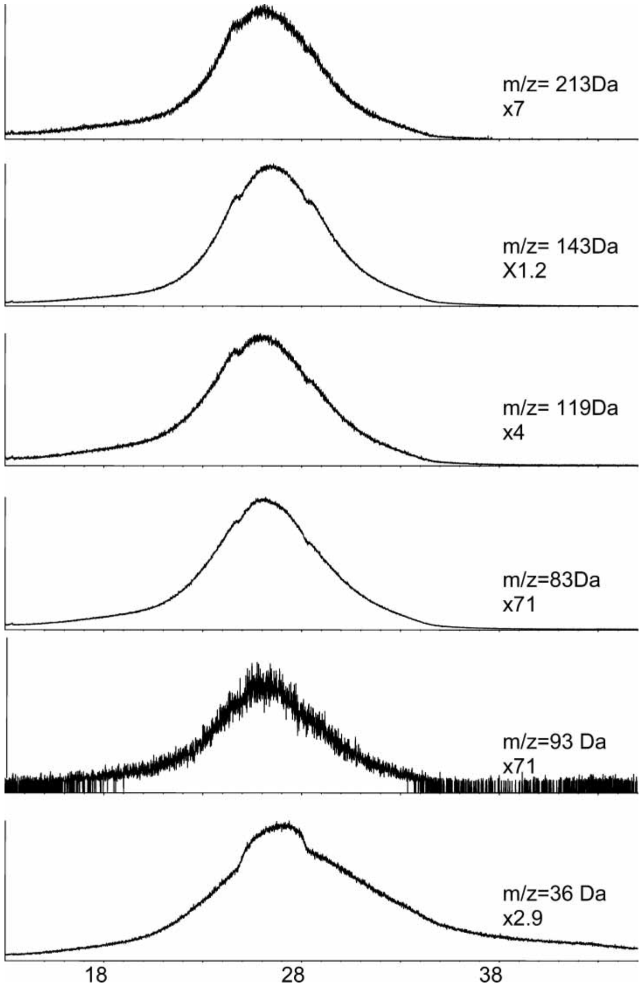

Figure 4. Evolution profiles of selected degradation products of Cl-PECH-4.2.

indicating a uniform thermal stability for each repeat unit. It may be concluded that as a result of chlorination, a uniform polymer backbone with lack of any double bond has been produced. Although repeat units with different number of chlorine atoms were detected, the thermal stability was more uniform indicating that the increase in number of chlorine atoms had no significant effect on thermal stability.

With the use of pyrolysis mass data, it can be concluded that chlorination of the unsaturated repeating units and abstraction of tertiary and secondary hydrogens had occurred first as regioselectivity of chlorination increases in the order tertiary $>$ secondary $>$ primary carbon atoms. As each repeat unit has about the same reactivity in case of PECH distribution of chlorine atoms was more uniform. In the case of PPO, as the reactivity of a chlorinated unit is greater than unchlorinated one, gathering of chlorine atoms on initially chlorinated units occurred the leaving rest of the units intact.

Conclusions

Pyrolysis analysis of chlorinated PPO and PECH indicated that chlorination of PECH yielded a more uniform structure having a uniform thermal stability.

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