

# The analysis of various polycarbonates by static secondary-ion mass spectrometry

J. Lub and G. H. Werumeus Buning

*Philips Research Laboratories, PO Box 80 000, 5600 JA Eindhoven, The Netherlands  
(Received 30 June 1989; accepted 25 August 1989)*

In this paper various polycarbonates are studied using static secondary-ion mass spectrometry. From the measurements information about the chemical structure of the polymers can be extracted. Apart from the structure of the repeat unit, also the structure of the polymer end-group and the distribution of monomers in a copolymer has been determined. Furthermore, the presence of cyclic oligomeric compounds in various polycarbonates has been established. A main-chain scission mechanism for the interaction of the primary ion beam with the polymers has been proposed, and with this mechanism it was possible to explain the structures of the most characteristic ions observed in the different types of spectra.

(Keywords: polycarbonate synthesis; polymer analysis; static secondary-ion mass spectrometry; cyclic polycarbonates; copolycarbonates; surface analysis; end-groups)

## INTRODUCTION

Static secondary-ion mass spectrometry (s.s.i.m.s.) is a relatively new technique for the analysis of polymers. Because of its high surface sensitivity it is an extremely useful technique for the characterization of the outermost surface region of polymeric material<sup>1-3</sup>. Information can be obtained not only on typical surface properties such as the presence of contaminants, but also on the polymer structure itself. In the case of polycarbonates, s.s.i.m.s. is capable of detecting end-groups originally present or formed after chemical treatments, which is more difficult with other analytical techniques<sup>4,5</sup>. Furthermore s.s.i.m.s., and in particular time-of-flight s.i.m.s. (t.o.f.-s.i.m.s.), which is capable of detecting ions with masses up to 10 000 amu, is one of the mass spectrometric techniques that can desorb rather large molecules or fragments of molecules, as ions<sup>6</sup>. In order to be able to observe ions with such a high mass, spectra have to be taken from thin layers of a polymer on silver (i.e. approximately a monolayer). From such spectra two types of ions can be distinguished: first, complete polymer molecules cationized by Ag<sup>+</sup>, and secondly, fragments of these polymer molecules, also cationized by Ag<sup>+</sup> (refs. 7, 8). The first type of ion is only important for polymers with low molecular weights within the detection range of the spectrometer ( $\bar{M}_n < 10\,000$ ). The second type, fragments of polymer molecules formed as a result of scission of the main chain due to the primary-ion bombardment, may still contain information on end-groups and on monomer sequence in the case of copolymers.

From the negative-ion spectra of pure poly(methyl methacrylate) (PMMA) and the positive-ion spectra of thin layers of PMMA on silver, it was concluded that characteristic enolate anions observed in the negative-ion spectra originate from end-groups either present originally or formed due to the primary-ion bombardment<sup>7,9,10</sup>. In this paper it will be discussed whether the same kind of information can be obtained for polycarbonates.

It was shown that the negative-ion spectra of thick layers of polycarbonates are much more characteristic

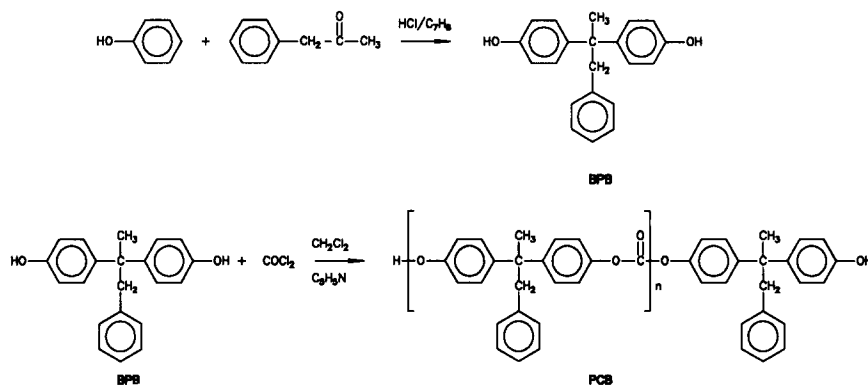
than the positive-ion ones<sup>4</sup>. Several phenolate-type anions were observed originating from the original end-groups or from the polymer backbone. The original end-groups of polycarbonates are derived from mono-functional aromatic hydroxy compounds such as phenol, *t*-butylphenol or isooctylphenol. These compounds are added during the synthesis of the polycarbonates to regulate the molecular weight. Furthermore, these end-groups protect the polymer against thermal degradation during moulding. Apart from s.s.i.m.s. the content of these end-groups can also be determined with h.p.l.c.<sup>11</sup>.

It can be expected for the positive s.s.i.m.s. spectra of thin layers of polycarbonate on silver that these spectra show fragments of the polymer molecules which contain information not only on the original end-groups, but also on the monomer sequence in the case of copolymers. Therefore, apart from the polycarbonate derived from the bisphenol of phenyl-2-propanone (PCB), we also synthesized a copolymer derived from bisphenol-A (BPA) and the bisphenol of phenyl-2-propanone (BPB). In order to obtain a random distribution of both bisphenols in the polymer, the reaction of these bisphenols with phosgene has to be performed in homogeneous solution because it is known that polymerizations, carried out under these conditions, are more successful in obtaining random structures than polymerizations in heterogeneous systems<sup>12-16</sup>. This copolymer as well as both homopolymers are of interest with regard to their stress optical properties<sup>17</sup>.

## EXPERIMENTAL

### *Instrumental*

The n.m.r. measurements were performed on a Bruker WP-80 SY spectrometer; the frequency used for <sup>1</sup>H n.m.r. is 80 MHz and for <sup>13</sup>C n.m.r. it is 20.13 MHz. Tetramethylsilane was used as internal standard. The i.r. spectra were taken on a Bruker R45 spectrometer. D.s.c. measurements were performed on a Perkin-Elmer DSC-2 (heating rate 20°C min<sup>-1</sup>). The time-of-flight



**Scheme 1** Synthesis of BPB from phenol and phenyl-2-propanone, and synthesis of PCB from BPB, phosgene and pyridine

static secondary-ion mass spectrometer used has been described before<sup>3,6,18,19</sup>.

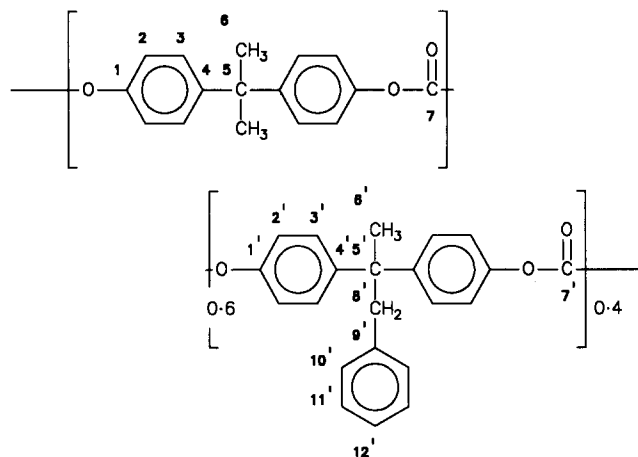
### Materials

The bisphenol-A polycarbonates used were CD 2000 (Bayer AG, FRG,  $M_w=20\,000$ ,  $M_n=9\,000$ ) and a secondary standard obtained from Aldrich ( $M_w=33\,800$ ,  $M_n=13\,400$ ). The  $T_g$  of these polymers is  $145^\circ\text{C}$ .

The bisphenol of phenyl-2-propanone was prepared in an analogous way to that of Islam *et al.*<sup>20</sup> (see Scheme 1) using 45 g phenyl-2-propanone (0.33 mol) and 125 g phenol (1.33 mol) in 100 ml toluene. Gaseous HCl was passed through the solution for 4 h at room temperature. After this the solution was allowed to stand for 5 days before the crystals formed were filtered off. After recrystallization (acetic acid/water=1/1) the yield of 4,4'-dihydroxydiphenyl-1-phenyl-2,2-propane (BPB) was 92%; m.p.  $222\text{--}225^\circ\text{C}$ .  $^1\text{H}$  n.m.r. (DMSO);  $\delta$  (ppm)=1.35 (s, 3H), 3.30 (s, 2H), 6.60–7.10 (m, 13H) and 9.15 (s, 2H). The presence of a small amount of *ortho* adduct can be observed using  $\text{CD}_3\text{OD}$  as solvent from a shoulder at the low-field side of the  $\text{CH}_3$  absorption. The  $^{13}\text{C}$  n.m.r. data are depicted in Table 1. I.r. (KBr): 3500, 3390, 3060–2940, 1610, 1590 and  $1510\text{ cm}^{-1}$ .

The polycarbonate of 4,4'-dihydroxydiphenyl-1-phenyl-2,2-propane (BPB) was synthesized for the greater part analogously to the method of Schnell<sup>21</sup> (Scheme 1). In the polycondensation 30.4 g BPB (0.1 mol) was reacted with 10.2 g phosgene in 100 g methylene chloride and 24 g pyridine (0.3 mol) at  $5\text{--}10^\circ\text{C}$  in a nitrogen atmosphere. The addition of phosgene was regulated with a mass-flow control unit: 9.5 g phosgene was added in 90 min; in the last 30 min 0.7 g was passed into the solution. In this way high molecular weights can be achieved. After this, 200 g methylene chloride was added to the viscous solution. The organic solution was washed with 10% HCl solution and  $\text{H}_2\text{O}$ , and then the polymer solution was poured into excess methanol. The white precipitate was purified by reprecipitation using methylene chloride/methanol. The amount of isolated polymer was 29 g (88%). The  $T_g$  of this polycarbonate PCB was  $165^\circ\text{C}$ . The molecular weight was determined using g.p.c., which was calibrated with polystyrene standards. The values found were  $M_w=61\,000$  and  $M_n=30\,000$ .  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ ):  $\delta$  (ppm)=1.55 (s, 3H), 3.40 (s, 2H), 6.50–6.80 (m, 2H) and 7.00–7.40 (m, 11 H). I.r. (film): 3120–2880, 1785, 1610, 1510, 1460, 890, 830 and  $700\text{ cm}^{-1}$ . The  $^{13}\text{C}$  n.m.r. data are given in Table 1.

**Table 1**  $^{13}\text{C}$  n.m.r. data of bisphenol-A (BPA), the bisphenol 4,4'-dihydroxydiphenyl-1-phenyl-2,2-propane (BPB), the polycarbonate PCA derived from BPA, the polycarbonate PCB derived from BPB and the copolymer from BPA and BPB (60/40), respectively. The numbering of the carbon atoms is given in the figure:



| Solvent       | DMSO   | DMSO         | $\text{CDCl}_3$ | $\text{CDCl}_3$ | $\text{CDCl}_3$   |
|---------------|--------|--------------|-----------------|-----------------|-------------------|
| Material      | BPA    | BPB          | PCA             | PCB             | Copolymer (60/40) |
| Carbon number |        |              |                 |                 |                   |
| 1             | 155.00 |              | 149.02          |                 | 149.03            |
| 1'            |        | 154.85       |                 | 149.19          | 149.18            |
| 2             | 114.84 |              | 120.31          |                 | 120.31            |
| 2'            |        | 114.40       |                 | 120.22          | 120.20            |
| 3             | 127.49 |              | 127.91          |                 | 127.92            |
| 3'            |        | 128.13       |                 | 127.47          | 127.46            |
| 4             | 141.41 |              | 148.27          |                 | 148.29            |
| 4'            |        | 139.60 (9'?) |                 | 146.98          | 146.95            |
| 5             | 41.10  |              | 42.58           |                 | 42.58             |
| 5'            |        | 47.13        |                 | 46.92           | 46.89             |
| 6             | 31.05  |              | 30.92           |                 | 30.92             |
| 6'            |        | 26.85        |                 | 27.25           | 27.24             |
| 7             |        |              | 152.08          |                 | 152.09            |
| 7'            |        |              |                 | 152.07          |                   |
| 8'            |        | 45.07        |                 | 47.98           | 47.90             |
| 9'            |        | 138.46 (4'?) |                 | 137.34          | 137.32            |
| 10'           |        | 127.02       |                 | 128.91          | 128.89            |
| 11'           |        | 130.43       |                 | 130.76          | 130.74            |
| 12'           |        | 125.95       |                 | 126.22          | 126.17            |

The copolymer of bisphenol-A (BPA) and the benzyl-substituted bisphenol BPB was synthesized analogously to the synthesis described above. The reaction was performed in a 1:1 mixture of methylene chloride/1,2-

dichloroethane in order to dissolve both bisphenols. In the reaction 0.06 mol BPA and 0.04 mol BPB were used. The overall composition of the copolymer was determined using  $^1\text{H}$  n.m.r.; a ratio of BPA/BPB = 60/40 was found. The  $T_g$  of this copolymer was  $156^\circ\text{C}$ ; the molecular weights  $M_w$  and  $M_n$ , relative to polystyrene, were 67 000 and 25 000, respectively. The  $^1\text{H}$  n.m.r.,  $^{13}\text{C}$  n.m.r. (see Table 1) and i.r. data are the sum of the spectra of PCA and PCB. From the three types of spectra no conclusions can be drawn with respect to the randomness of the structure of the copolymer.

The reaction between PCA (Aldrich) and n-butylamine was performed by stirring a mixture of 2.5 g of the polymer (10 mmol of repeat units) and 0.1 ml of n-butylamine (1 mmol) in 50 ml methylene chloride. The reaction was followed by i.r. (spin-coated layer on  $\text{CaF}_2$ ). After approximately 8 h the ratio between the peaks at  $1770\text{ cm}^{-1}$  (carbonate  $\text{C}=\text{O}$ ) and at  $1710$  and  $1730\text{ cm}^{-1}$  (urethane  $\text{C}=\text{O}$ ) was constant and the reaction was assumed to be complete.

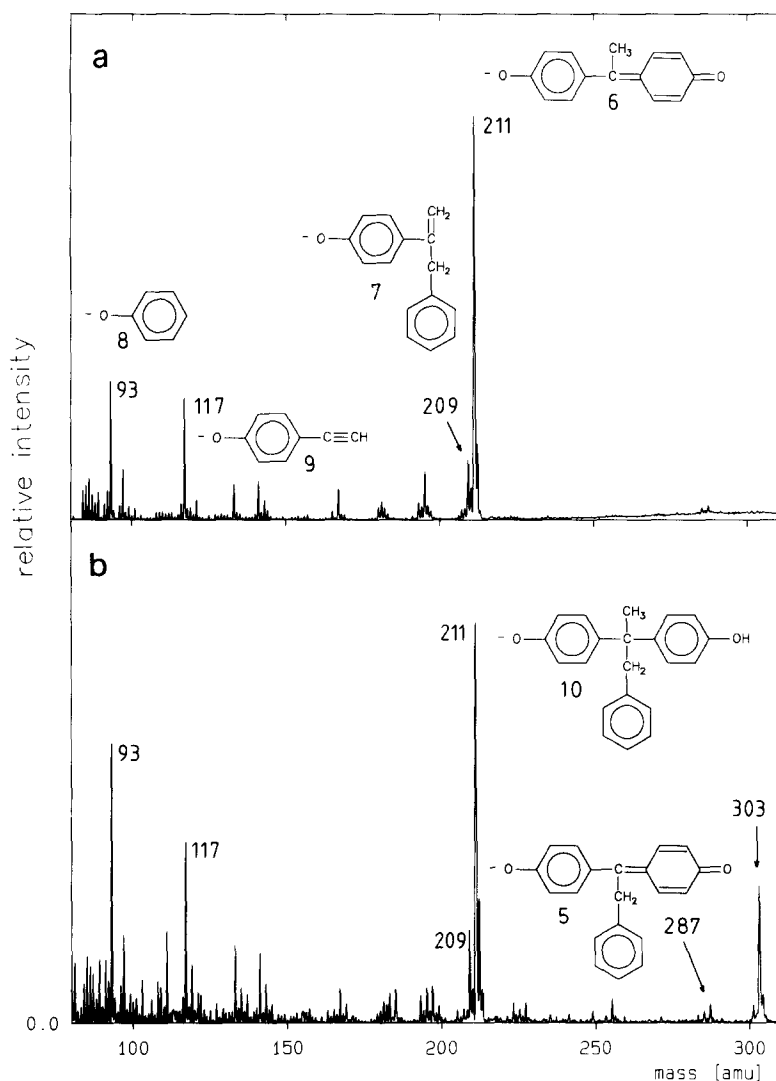
The s.s.i.m.s. samples were prepared by spin-coating the polymers from chloroform and methylene chloride solutions. The layer thickness was varied by varying the concentrations<sup>4,7,8</sup>. BPB was spin-coated from ethanolic solution.

## RESULTS AND DISCUSSION

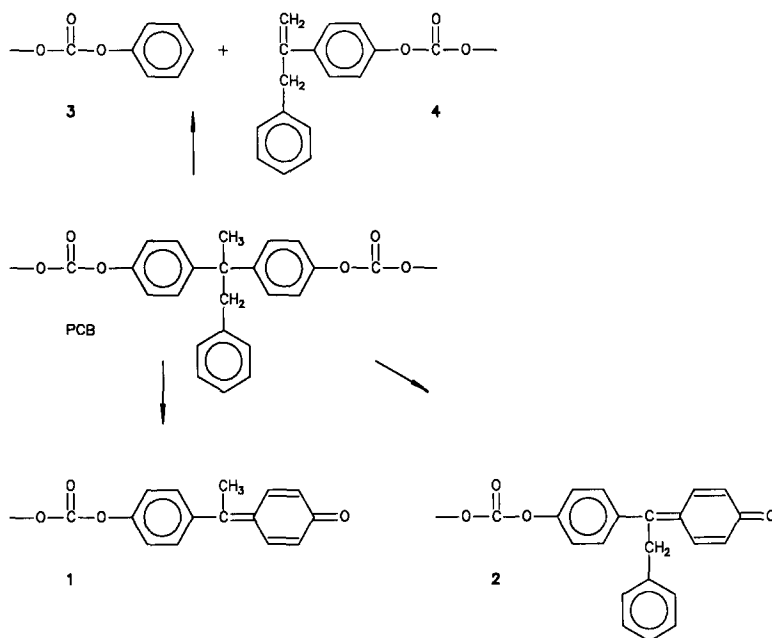
### The negative-ion spectrum of the polycarbonates

Figure 1A shows the negative-ion spectrum of PCB. The spectrum was recorded beginning at 80 amu because below this value only relatively intense signals are observed due to  $\text{O}^-$ ,  $\text{OH}^-$ ,  $\text{C}_n^-$  and  $\text{C}_n\text{H}^-$ , which do not contain structural information<sup>4</sup>. The most intense peaks in the mass range shown in Figure 1A are found at 93, 117 and 211 amu. These peaks are also observed in the negative-ion spectrum of PCA<sup>4</sup>.

Scheme 2 shows a proposed mechanism for chain scission of PCB due to the primary-ion bombardment. The weakest bonds in the polymer are the carbonate bond and the C-C bonds to the central carbon atom of the bisphenol unit. After homolytic chain scission, in which the carbonate bond breaks and a benzyl radical is lost, the new chain end 1 is formed. From this chain end anion 6, observed at 211 amu (Figure 1A), will originate. Instead of loss of a benzyl radical, loss of a methyl radical will give rise to chain end 2. Anion 5 (see Figure 1B) at 287 amu, which is expected to be formed in the same way as the one at 211 amu from structure 1, can hardly be observed in Figure 1A. Apparently splitting off of the benzyl group is preferred to splitting off of the methyl



**Figure 1** Negative s.s.i.m.s. spectra in mass range 80–320 amu (and structures of the ions formed) of the surface of a thick layer of PCB (A) and of a layer of BPB (B) on silica



Scheme 2 Mechanism for the formation of new chain ends of PCB due to the primary-ion bombardment

group. The other remnant of the carbonate group after formation of **1** or **2** may lose carbon monoxide, resulting in a phenoxide-type radical, which may also form structures **1** or **2** after loss of a benzyl or methyl radical, respectively. Another reaction path is elimination of chain end **3** derived from phenol with the simultaneous formation of chain end **4**. These chain ends will give rise to the anions **8**, observed at 93 amu, and **7**, at 209 amu, respectively. This last ion may lose toluene and hence form the ion **9** observed at 117 amu.

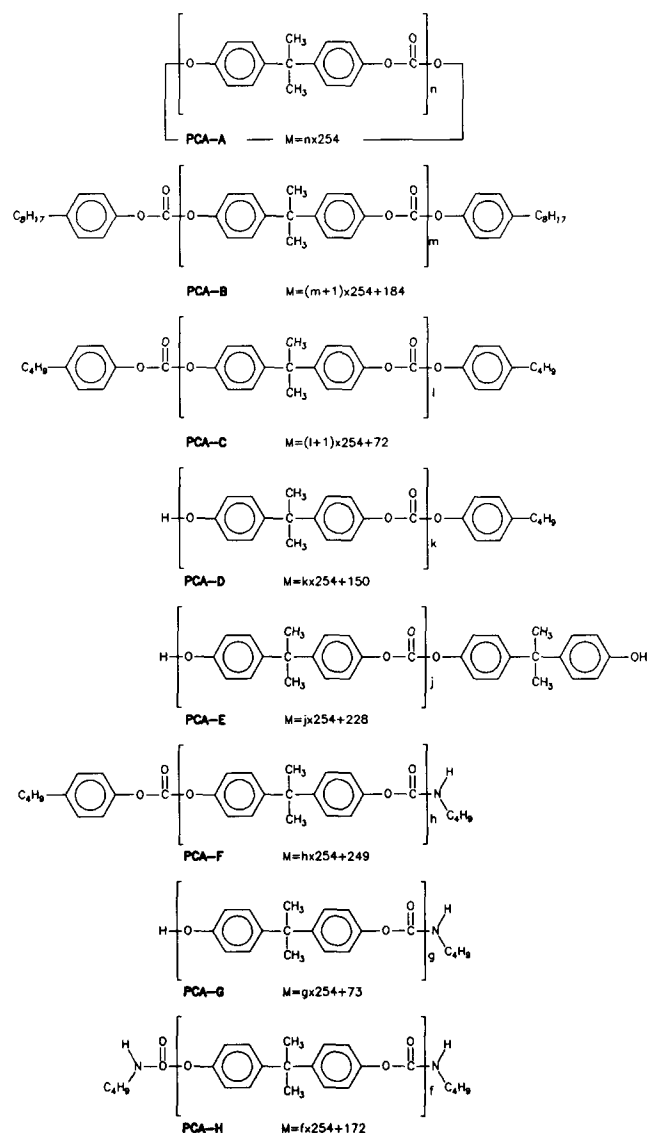
In the negative-ion spectrum of PCA the peak at 211 amu is also the most intense one in this mass range<sup>4</sup>. In that case loss of methane instead of toluene will lead to structure **1**. Analogous to this a structure will be formed from PCA in which the benzyl group in chain end **4** is replaced by a methyl group, leading to an anion at 133 amu. After loss of methane from this ion, the ion observed at 117 amu is formed<sup>4</sup>.

The negative-ion spectrum of the copolymer derived from BPA and BPB (not shown) is not very characteristic for this copolymer. This can be expected because the negative-ion spectra of both homopolymers do not differ very much.

During the synthesis of PCB and the copolymer, no monofunctional phenol was used because this facilitates the synthesis and promotes the achievement of sufficiently high-molecular-weight polymers. Therefore the chain ends of PCB, which are derived from BPB, and the chain ends of the copolymer, which are derived from BPA and BPB, have OH-terminated bisphenol end-groups. They should give rise to peaks at 303 and 227 amu due to the anions of both bisphenols. Surprisingly, these peaks are not observed.

#### The effect of end-groups on surface composition

The negative-ion spectra of spin-coated layers of PCA with end-groups derived from isooctylphenol (structure PCA-B, see Scheme 3) or *t*-butylphenol (structure PCA-C, see Scheme 3) show the isooctylphenolate anion (205 amu) or *t*-butylphenolate anion (149 amu),



Scheme 3 Types of polycarbonate of which the low-molecular-weight species can be observed in the spectra of Figure 2

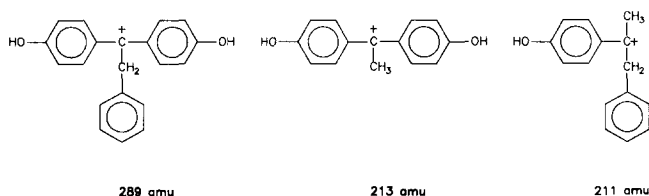
respectively<sup>4</sup>. In contrast to the polar OH-terminated end-groups of PCB and the copolymer, these polymers have relatively non-polar end-groups. In order to find out if the polarity of the end-groups influences the s.s.i.m.s. spectra, we prepared a mixture of polycarbonate molecules with structures PCA-D, -E, -F, -G and -H (see Scheme 3) by reaction of the t-butylphenol-terminated polycarbonate with n-butylamine<sup>4,22,23</sup>. The negative-ion spectrum of a spin-coated layer of this mixture (not shown here) was nearly identical with that of PCA-C (thus only the end-group derived from t-butylphenol could be detected at 149 amu). The bisphenolate-A anion or n-butylcarbamate anions are not observed. Previous work revealed that, if the polar end-groups are present at the surface, they are indeed observed in the s.s.i.m.s. spectra<sup>4,5</sup>. From this it can be concluded that apparently during the spin-coating process, which is used to prepare the samples, the relatively polar chain ends derived from species such as BPA, BPB and amines enter into the bulk of the material in order to keep the surface tension of the polymer film low. These chain ends can therefore not be detected by s.s.i.m.s. because of its low analysis depth ( $\pm 10 \text{ \AA}$ )<sup>24</sup>.

#### The s.s.i.m.s. spectra of BPB

Comparison of the negative-ion spectra of PCA and BPA revealed that both spectra are similar, with the exception of the bisphenolate-A anion detected at 227 amu in the spectrum of BPA<sup>4</sup>. The negative-ion spectra of BPB (Figure 1B) and PCB (Figure 1A) also show similarity. In the spectrum of BPB the bisphenolate anion 10 is observed at 303 amu. The other anions may be formed from BPB in a similar way as outlined in Scheme 2. In this case an OH group should be read instead of a carbonate group. The bisphenolate anion (303 amu) may also lose methane, toluene, phenol or p-phenylisopropenylphenol to form the anions 5, 6, 7 and 8, respectively.

Only little structural information can be obtained from the positive-ion spectra of polycarbonates due to preferential formation of ions from the aromatic rings of the bisphenol units. Contrary to this, the positive-ion spectra of bisphenols do show characteristic ions<sup>4</sup>. PCB and BPB behave similarly. In the case of BPB (spectrum not shown), ions were observed at 289, 213 and 211 amu. The corresponding ion structures are depicted in Scheme 4.

The intensity of the ion at 289 amu was about 3% of that of the ion at 213 amu, which was only about twice as intense as the ion at 211 amu. Furthermore, comparison of the intensities of the peaks at 211 and 287 amu in the negative-ion spectra of PCB (Figure 1A) and BPB (Figure 1B) also revealed that loss of the methyl group is by far preferred to loss of the methyl group from the central C atom of the BPB units. The intensity of the peak at



Scheme 4 Characteristics ions observed in the positive s.s.i.m.s. spectrum of BPB

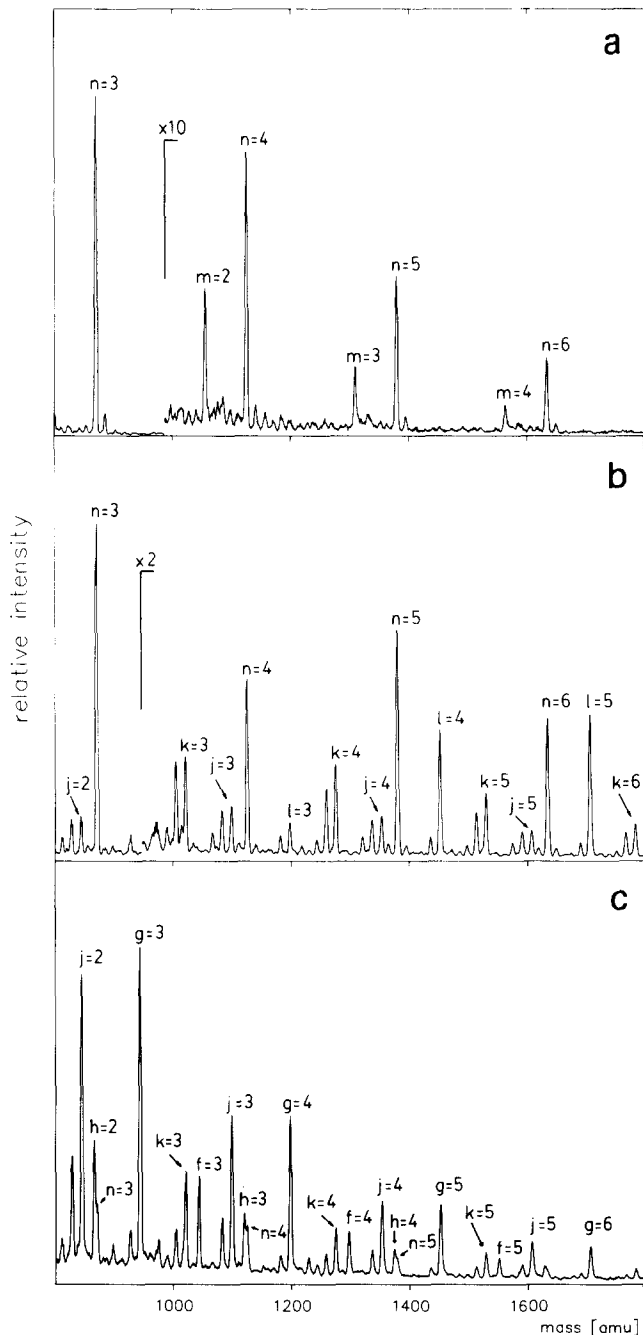


Figure 2 Positive s.s.i.m.s. spectra in the mass range 800–1800 amu of a thin layer of Bayer CD 2000 (A), Aldrich secondary-standard polycarbonate (B) and Aldrich secondary-standard polycarbonate after reaction with butylamine (C), on silver etched by nitric acid

211 amu in the negative-ion spectrum of BPA is about 30% of that of its bisphenolate anion (227 amu)<sup>4</sup>. In the case of BPB this peak is about three times as intense as that of the bisphenolate anion (303 amu). All these results show the relative ease of benzyl loss from the BPB structure. This benzyl loss will also play a role in the interpretation of the positive-ion spectra on silver of PCB and copolymers containing the BPB structure, as will be described in the next sections.

#### The positive-ion spectra of various samples of PCA on silver

Figures 2A, 2B and 2C show the spectra of thin layers of PCA with chain ends derived from isooctylphenol (Bayer CD-2000), chain ends derived from t-butylphenol

(Aldrich) and chain ends derived from n-butylamine and BPA (see previous section), respectively.

In *Figure 2A* two types of polymer molecules can be distinguished. These molecules are cationized by  $\text{Ag}^+$ , which means that the mean mass of the ions is 108 amu higher than that of the polymer molecules as outlined in *Scheme 3*. At low mass range the two peaks with  $\Delta m = 2$  due to both Ag isotopes can be distinguished. The first type of peak is due to cyclic carbonates with structure PCA-A (see *Scheme 3*). Especially the molecule with  $n = 3$  causes a very intense peak. This molecule is apparently present in excess among other low-molecular-weight species. The formation of cyclic, oligomeric products during the synthesis of polycarbonates under normal reaction conditions is not much reported in the literature. A few papers deal with cyclic polycarbonates, which are obtained under special conditions. The cyclic tricarboxylate of bis(4-hydroxyphenyl)-1,1-dichloroethylene can be obtained in quantitative yield when a tertiary amine is added to a solution of the corresponding linear polycarbonate<sup>25</sup>. Furthermore, cyclic tetrameric carbonates, derived from different bisphenols, can be synthesized under high dilution conditions<sup>26</sup>. Horbach *et al.*<sup>27</sup> have reported the formation of high-molecular-weight cyclic carbonates during interfacial condensation polymerization of bis-chloroformates of BPA with BPA. The formation of cyclic compounds is very well known for polyesters such as poly(ethylene terephthalate) (PET)<sup>28-30</sup>. The dominant cyclic trimer at the surface of this polymer was also observed using s.s.i.m.s.<sup>31</sup>.

The second type of peak in *Figure 2A* is due to linear polymer molecules with two chain ends derived from isooctylphenol (PCA-B). No indication is found for the formation of fragmentation products of these macromolecules due to the primary-ion bombardment. Hence the spectrum only gives information on the structures of the low-molecular-weight species present in the polymer sample.

In *Figure 2B* the same two types of molecules are observed as in *Figure 2A*. In this case structure PCA-B is of course replaced by structure PCA-C. Furthermore, two other types of polymer molecules are detected as cationized structures. Structures PCA-D and PCA-E can be assigned to these polymer molecules. They contain chain ends derived from t-butylphenol on one end and BPA on the other end, and from BPA on both ends, respectively. Apparently, during the synthesis of this polymer not all the chain ends were terminated by t-butylphenol or part of the carbonate bonds are hydrolysed on the silver surface (see further). The peaks due to structures PCA-C are accompanied by peaks of relatively low intensity with masses 16 amu lower. This was not observed in the case of PCA-B. Therefore these peaks are probably not formed by loss of methane from the repeat unit, but by loss of methane from the chain ends derived from t-butylphenol (i.e. forming a chain end derived from isopropenylphenol). The peaks due to structure PCA-D are also accompanied by peaks with a mass of 16 amu lower; however, they are more intense. These peaks can be assigned to cationized species of PCA-D in which methane is lost. Because this methane loss is not found for structures PCA-A and PCA-B, the most plausible explanation here is that methane is lost from the chain end derived from BPA, hence forming structure 1 of *Scheme 2*. In the case of structure PCA-E fragmentation products are formed not only by loss of

one molecule of methane ( $\Delta m = 16$  amu) but also by loss of two molecules of methane ( $\Delta m = 32$  amu). This is due to the fact that there are now two chain ends derived from BPA. The intensities of these peaks vary from sample to sample. Probably the (uncontrolled) interaction of silver with the chain ends derived from BPA plays a role in the elimination of methane.

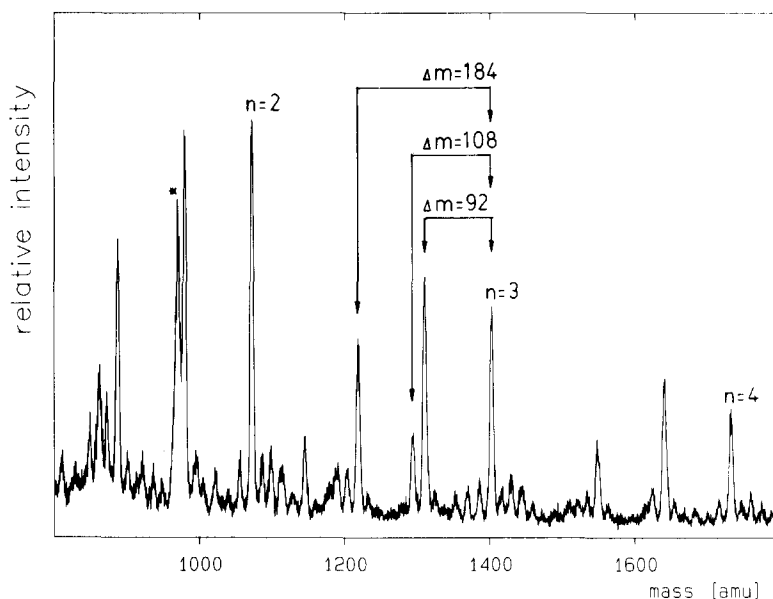
*Figure 2C* shows the positive-ion spectrum of a thin layer of a mixture of the polymer molecules with structures PCA-D to PCA-H. This mixture was obtained after reaction of the polycarbonate with end-groups derived from t-butylphenol and n-butylamine. From this example it is clear that the spectra of thin polymer layers on silver give more information on the structures of the end-groups than do the negative-ion spectra of thick polymer samples, in which the end-group derived from BPA and n-butylamine could not be observed.

If the sample of the t-butyl-terminated polycarbonate, which gives rise to the spectrum of *Figure 2B*, is prepared with freshly vapour-deposited silver, the intensities of the peaks due to structures PCA-D and PCA-E increase significantly relative to those of structures PCA-A and PCA-C. In the case of the sample of *Figure 2A*, new structures are observed with one chain end or two chain ends derived from BPA. Apparently the carbonate bond is broken or hydrolysed by this grade of silver prior to or during the primary-ion bombardment. Use will be made of this phenomenon in the next section.

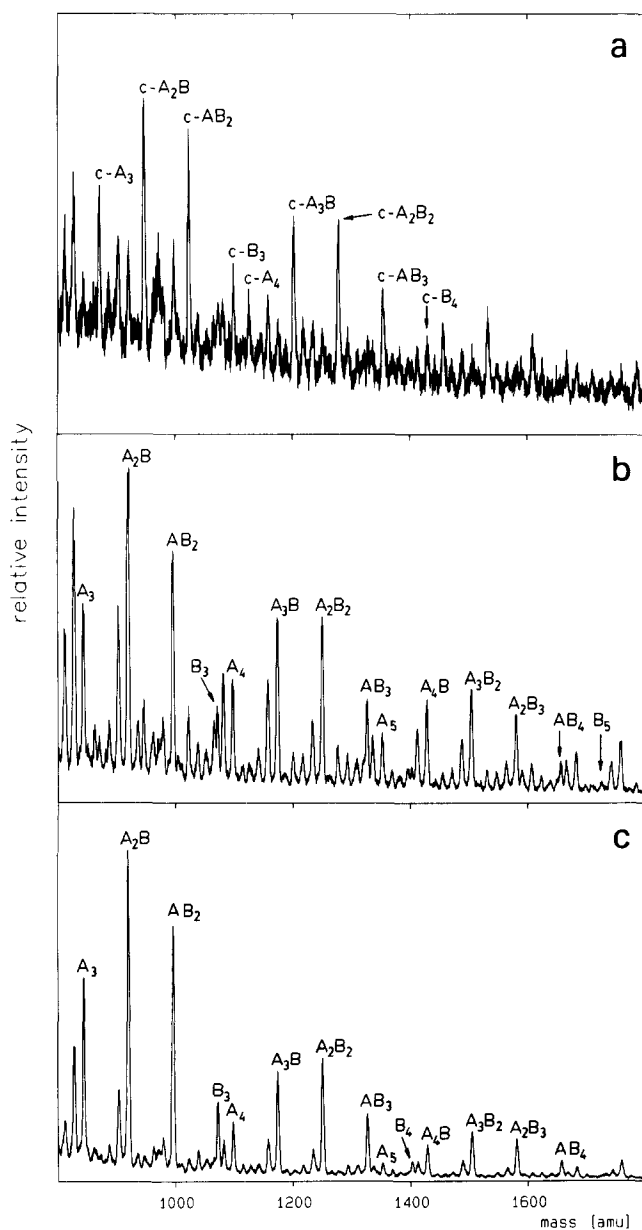
#### *The positive-ion spectra of PCB and a copolymer derived from BPA and BPB, on silver*

Only very weak signals can be obtained from BPB on silver etched by nitric acid. Using vapour-deposited silver, low-molecular-weight species are observed (*Figure 3*). The chain ends formed by interaction with silver and the original chain ends are derived from BPB (see *Scheme 1*) and have masses of  $(n+1) \times 330.4 - 26$  amu. Owing to the cationization by  $\text{Ag}^+$  the observed ions have masses of  $(n+1) \times 330.4 + 82$  amu. Those chain ends may lose toluene or methane to form species in which one of the chain ends has structure 1 or 2 of *Scheme 2*, respectively. The polymer chains with one chain end with structure 2 ( $\Delta m = 16$  amu) can hardly be observed as cationized ions in *Figure 3*. Contrary to this, the one with structure 1 ( $\Delta m = 92$  amu) gives a relatively intense signal. As argued before, the loss of toluene from the chain end derived from BPB is much preferred to loss of methane. After loss of two molecules of toluene or loss of one molecule of toluene and one molecule of methane, structures are observed cationized by  $\text{Ag}^+$  with  $\Delta m = 184$  and 108 amu, respectively. Structures in which more than two molecules of toluene are lost are not observed. This again indicates that toluene loss is only possible from the chain ends, just as in the case of methane loss from chain ends derived from BPA.

*Figure 4A* shows the spectrum of the copolymer derived from 60% of BPA and 40% of BPB on silver etched with nitric acid. The most intense signals are due to cyclic structures. These structures can be described by  $c\text{-A}_x\text{B}_y$ ;  $x$  is the amount of units derived from BPA (A) and  $y$  from BPB (B). There are  $x+y$  carbonate bonds, hence the mass of a cyclic structure is  $x + 254.3 + y \times 330.4$ . Owing to the cationization by  $\text{Ag}^+$ , these molecules are observed with a mean mass of  $x \times 254.3 + y \times 330.4 + 108$  amu. On vapour-deposited silver (*Figures 4B* and



**Figure 3** Positive s.s.i.m.s. spectrum in the mass range 800–1800 amu of a thin layer of PCB on freshly vapour-deposited silver. The peak marked with the asterisk is due to  $\text{Ag}_9^+$



4C) these cyclic structures can hardly be observed. The chain scission induced by the freshly deposited silver forms low-molecular-weight structures with chain ends derived from both bisphenols, which are detected much more intensely than the cyclic species. Because the chain ends as well as the repeat units of these macromolecules are derived from both bisphenols, the individual polymer chains can be described by  $A_xB_y$ . There are  $x + y - 1$  carbonate bonds; hence the mass of a chain is  $x \times 254.3 + y \times 330.4 - 26$ . Owing to the cationization by  $\text{Ag}^+$ , these molecules are observed with a mass of  $x \times 254.3 + y \times 330.4 + 82$  amu. The  $A_xB_y$  notation is used in Figures 4B and 4C. The spectrum of Figure 4C was obtained from a sample prepared by spin-coating a solution with four times lower concentration compared to the sample of Figure 4B. Lower concentrations resulted in very noisy spectra. In the spectra of Figures 4B and 4C fragmentation products are observed. They are due to loss of methane from  $A_xB_y$  ( $\Delta m = 16$  amu), to loss of toluene from  $A_{x-1}B_{y+1}$  ( $\Delta m = 92$  amu) or to a combination of these processes. The intensity of these peaks increases relative to those of the peaks of the original species going from the sample of Figure 4C to the thicker sample of Figure 4B. Apparently more fragmentation products are formed as the sample thickness increases.

The theoretical ratio of polymer molecules with  $x + y = 3, 4$  and  $5$ , calculated for this copolymer assuming a random statistical distribution of both bisphenol units, is depicted in column 2 of Table 2. Columns 4 and 6 show the intensity ratios of the peaks due to structures  $A_xB_y$ , obtained from Figures 4B and 4C, respectively. Because it can be assumed that toluene loss is preferred to methane loss (see previous sections), the intensity distributions of the peaks due to the fragmentation products are compared with those of the original species

**Figure 4** Positive s.s.i.m.s. spectra in the mass range 800–1800 amu of a thin layer of a random copolymer derived from 60% BPA and 40% BPB on silver etched by nitric acid (A), on freshly vapour-deposited silver (B) and on freshly vapour-deposited silver but with a four times lower polymer concentration of the spin-coating solution (C)

**Table 2** Calculated and observed (Figure 4) peak intensities for the copolycarbonate derived from BPA and BPB (60/40). Column 2: statistical distribution of peak intensities calculated for trimers, tetramers and pentamers with the composition outlined in column 1. Column 3: peak intensities for cyclic species with mass  $x \times 254.3 + y \times 330.4 + 108$  amu, obtained from Figure 4A. Columns 4 and 6: peak intensities for linear species with mass  $x \times 254.3 + y \times 330.4 + 82$  amu, obtained from Figures 4B and 4C, respectively. Columns 5 and 7: peak intensities for linear species with mass  $x \times 254.3 + y \times 330.4 - 10$  amu, obtained from Figures 4B and 4C, respectively. For all three  $n$ -mers the peak intensities are normalized to the highest peak with intensity = 1.00

| Polymer composition<br>$A_xB_y$ | Peak intensity |           |           |      |           |      |
|---------------------------------|----------------|-----------|-----------|------|-----------|------|
|                                 | Calculated     | Figure 4A | Figure 4B |      | Figure 4C |      |
| 1                               | 2              | 3         | 4         | 5    | 6         | 7    |
| $A_3B_0$                        | 0.50           | 0.60      | 0.57      | –    | 0.62      | –    |
| $A_2B_1$                        | 1.00           | 1.00      | 1.00      | 1.00 | 1.00      | 1.00 |
| $A_1B_2$                        | 0.67           | 0.80      | 0.74      | 0.61 | 0.79      | 0.63 |
| $A_0B_3$                        | 0.15           | 0.30      | 0.24      | 0.24 | 0.23      | 0.25 |
| $A_4B_0$                        | 0.38           | 0.40      | 0.60      | –    | 0.45      | –    |
| $A_3B_1$                        | 1.00           | 1.00      | 1.00      | 0.97 | 0.93      | 0.95 |
| $A_2B_2$                        | 1.00           | 0.90      | 1.00      | 1.00 | 1.00      | 1.00 |
| $A_1B_3$                        | 0.44           | 0.60      | 0.48      | 0.60 | 0.52      | 0.75 |
| $A_0B_4$                        | 0.03           | 0.20      | 0.07      | 0.19 | 0.05      | 0.28 |
| $A_5B_0$                        | 0.22           |           | 0.50      | –    | 0.25      | –    |
| $A_4B_1$                        | 0.65           |           | 0.84      | 0.78 | 0.63      | 0.50 |
| $A_3B_2$                        | 1.00           |           | 1.00      | 1.00 | 1.00      | 0.87 |
| $A_2B_3$                        | 0.66           |           | 0.74      | 0.90 | 0.67      | 1.00 |
| $A_1B_4$                        | 0.22           |           | 0.29      | 0.41 | 0.32      | 0.55 |
| $A_0B_5$                        | 0.03           |           | 0.03      | 0.13 | 0.05      | 0.15 |

with a mass of 92 amu higher. These intensity distributions are depicted in columns 5 and 7. Obviously peaks with  $\Delta m = 92$  amu are not observed for  $y = 0$ . These distributions reflect more or less those of the original species. Especially the spectrum of Figure 4B reveals structures with a mass of 32 amu lower than that of original species  $A_xB_y$  or a mass 108 amu lower than that of original species  $A_{x-1}B_{y+1}$ . These peaks may originate after loss of two molecules of methane or after loss of one molecule of methane and one molecule of toluene, respectively. Thus methane loss also plays a role for these macromolecules with chain ends derived from the bisphenols used. We observed the same behaviour for the homopolymers with unprotected chain ends derived from the bisphenols. Comparison of the distribution of the molecular species in columns 4 and 6 of Table 2 reveals that in the case of the sample used in Figure 4B with the relatively high amount of fragmentation products (column 4), the amount of structures  $A_xB_0$  ( $x = 4, 5$ ) is much higher than in the case of the sample used in Figure 4C with the relatively low amount of fragmentation products (column 6), and also of the calculated distribution. This can be explained by the fact that the fragmentation products originate from the cationized structures of the molecular species  $A_xB_y$ . Owing to the fact that toluene loss from chain ends derived from BPB is preferred to methane loss from BPB and BPA, the peak intensities due to structures  $A_xB_0$  are less affected. In the case of the trimer ( $x + y = 3$ ), the difference between the results from Figures 4B and 4C is small. The origin of this effect is not clear.

For quantitative determinations, spectra should be taken under circumstances where the formation of fragmentation products is relatively unimportant. Com-

parison of the distribution of  $A_xB_y$  species obtained from Figure 4C (column 6 of Table 2) with the theoretical distribution (column 2) reveals that this copolymer contains the bisphenol units randomly distributed. This conclusion can also be drawn from the distribution of cyclic structures obtained from Figure 4A and shown in column 3 of Table 2. Owing to the low signal-to-noise ratio, only the results for the trimers and tetramers are given although these results are less reliable than those from the other two figures.

## CONCLUSIONS

From these s.s.i.m.s. measurements of polycarbonates, the following conclusions can be drawn.

The structure of the polycarbonate chain ends can be determined.

Polar end-groups are hardly present at the surfaces of thick spin-coated polymer layers.

A main-chain scission mechanism for the interaction of the primary-ion beam with the polymer has been proposed and this mechanism explains the major part of the characteristic ions observed in the different kinds of spectra.

The interaction of the polymer with the underlying silver layer in the case of spectra of thin polymer layers is very much dependent on the properties of the silver layer.

The distribution of bisphenol units in a copolycarbonate can be determined.

The presence of cyclic oligomeric structures is a common phenomenon in polycarbonates.

## ACKNOWLEDGEMENTS

The authors wish to thank Professor A. Benninghoven of the Physics Institute at The University of Münster for giving us the opportunity to carry out the s.s.i.m.s. measurements. R. Kock and M. Deimel of the same Institute are thanked for performing the s.s.i.m.s. measurements and F.C.B.M. van Vroonhoven for preparing most of the s.s.i.m.s. samples.

## REFERENCES

- 1 Briggs, D. *Polymer* 1984, **25**, 1379
- 2 Lub, J. Proceedings SIMS VI, (Eds. A. Benninghoven, A. Huber and H. W. Werner), Wiley, Chichester, 1988, p. 1033
- 3 Lub, J., van Velzen, P. N. T., van Leyen, D., Hagenhoff, B. and Benninghoven, A. *Surf. Interface Anal.* 1988, **12**, 53
- 4 Lub, J., van Vroonhoven, F. C. B. M., van Leyen, D. and Benninghoven, A. *Polymer* 1988, **29**, 998
- 5 Lub, J., van Vroonhoven, F. C. B. M., Bruninx, E. and Benninghoven, A. *Polymer* 1989, **30**, 40
- 6 Bletsos, I. V., Hercules, D. M., van Leyen, D. and Benninghoven, A. *Macromolecules* 1987, **20**, 407
- 7 Lub, J. and Benninghoven, A. *Org. Mass Spectrom.* 1989, **24**, 164
- 8 Lub, J., van Leyen, D. and Benninghoven, A. *Polym. Commun.* 1989, **30**, 74
- 9 Lub, J., van Vroonhoven, F. C. B. M., van Leyen, D. and Benninghoven, A. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 2071
- 10 Hearn, M. J. and Briggs, D. *Surf. Interface Anal.* 1988, **11**, 198
- 11 Horbach, A., Freitag, D. and Müller, H. *Angew. Makromol. Chem.* 1985, **136**, 1
- 12 Schnell, H. in 'Chemistry and Physics of Polycarbonates', (Eds. H. F. Mark and E. H. Immergut), Wiley-Interscience, New York, 1964, p. 53
- 13 Ikeda, K. and Sekine, Y. *Ind. Eng. Chem., Prod. Res. Dev.* 1973, **12**, 202



- |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>14 Adam, G. A., Parsons, I. W. and Haward, R. N. <i>Polymer</i> 1975, <b>16</b>, 433</p> <p>15 Al-Faize, M. M., Adam, G. A. and Al-Issa, M. <i>Polym. J.</i> 1980, <b>12</b>, 225</p> <p>16 Adam, G. A., Haward, R. N. and Parsons, I. W. <i>Eur. Polym. J.</i> 1976, <b>12</b>, 279</p> <p>17 Werumeus Buning, G. H., Wimberger-Friedl, R., Janeschitz-Kriegl, H. and Ford, T. M. in 'Integration of Fundamental Polymer Science and Technology', (Eds. L. A. Kleintjens and P. J. Lemstra), Elsevier, London, 1988, Vol. 2, p. 405</p> <p>18 Steffens, P., Niehuis, E., Friese, T. and Benninghoven, A. in 'Ion Formation from Organic Solids', (Ed. A. Benninghoven), Springer, Berlin, 1983, Vol. 25, p. 111</p> <p>19 Steffens, P., Niehuis, E., Friese, T., Greitendorf, D. and Benninghoven, A. <i>J. Vac. Sci. (A)</i> 1985, <b>3</b>, 1322</p> <p>20 Islam, A. M., Hassan, E. A., Rashad, M. E. and Wassel, M. M. <i>Egypt. J. Chem.</i> 1977, <b>20</b>, 483</p> | <p>21 Schnell, H., in ref. 12, p. 32</p> <p>22 Caldwell, J. R. and Jackson, W. J. <i>J. Polym. Sci. (C)</i> 1966, <b>24</b>, 15</p> <p>23 See ref. 12, Ch. 5</p> <p>24 Hearn, M. J., Briggs, D., Yoon, S. C. and Ratner, B. D. <i>Surf. Interface Anal.</i> 1987, <b>10</b>, 384</p> <p>25 Hallgren, J. E. and Matthews, R. O. <i>J. Polym. Sci., Polym. Chem. Edn.</i> 1979, <b>17</b>, 3781</p> <p>26 Schnell, H. and Bottenbruch, L. <i>Makromol. Chem.</i> 1962, <b>57</b>, 1</p> <p>27 Horbach, A., Vernaleken, H. and Weirauch, K. <i>Makromol. Chem.</i> 1980, <b>181</b>, 111</p> <p>28 Ha, W. S. and Choun, Y. K. <i>J. Polym. Sci., Polym. Chem. Edn.</i> 1979, <b>17</b>, 2103</p> <p>29 Cimecioglu, A. L., Zeronian, S. H., Alger, K. W., Collins, M. J. and East, G. C. <i>J. Appl. Polym. Sci.</i> 1986, <b>32</b>, 4719</p> <p>30 Jabarin, S. A. and Balduff, D. C. <i>Liq. Chromatogr.</i> 1982, <b>5</b>, 1825</p> <p>31 Briggs, D. <i>Surf. Interface Anal.</i> 1986, <b>8</b>, 133</p> |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|