Copolymerization of Propene Oxide with Carbon Dioxide: Aselective Incorporation of Propene Oxide into the Polycarbonate Chains, determined by 100 MHz ^{13}C N.M.R. Spectroscopy

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^{13}C N.m.r. spectroscopy has established that propene oxide–carbon dioxide copolymers prepared with diethylzinc-based catalysts can contain significant amounts of inverted propene oxide units, in contrast to the exclusively head-to-tail structures reported previously.

We describe a hitherto unreported structure for propene oxide–carbon dioxide copolymers. These aliphatic polycarbonates,[1] which until now could be represented by the formula (**1**), represent one of the few catalytic uses of carbon dioxide, a topic attracting considerable interest at present.[2]

The structure of (**1**) has been described[1] as simple and well-ordered, based on the observation[3] of a four-line ^{13}C n.m.r. spectrum, corresponding to the four distinct carbon atoms. This structure arises from selective attack by the growing chain on the methylene carbon atom in the propene oxide monomer. A second report[4] noted, without comment, two ^{13}C n.m.r. signals for the carbonate carbon atom of a propene oxide–carbon dioxide copolymer. In contrast, we find that propene oxide–carbon dioxide copolymers prepared under three sets of conditions† show a complex and almost identical pattern of lines for the carbonate carbon atom (see Figure 1). Integration establishes a ratio of 1.03 ± 0.02 propene oxide to carbon dioxide units in the chain, and the absence of signals in the range δ 142—152 eliminates the possibility of adjacent carbon dioxide units (*cf.* the shift of δ 148.3 reported for the carbonate carbon atom in EtO·CO·O·CO·OEt). The materials obtained are therefore defined as alternating copolymers.

$$-[\mathrm{CHMeCH_2O \cdot CO \cdot O}-]_n$$

(1)

$$-[\mathrm{CH_2CHMeO \cdot CO \cdot OCH_2CHMeO \cdot CO \cdot O}-]$$

head-to-tail, HT

$$-[\mathrm{CH_2CHMeO \cdot CO \cdot OCHMeCH_2O \cdot CO \cdot O}-]$$

head-to-head, HH

$$-[\mathrm{CHMeCH_2O \cdot CO \cdot OCH_2CHMeO \cdot CO \cdot O}-]$$

tail-to-tail, TT

The observed carbonate carbon atom resonances can be described as three main groups of peaks, labelled HT, HH, and TT, each containing fine structure, and an additional minor peak labelled HT′. The main groups of peaks are believed to be due to the units shown below structure (**1**), which arise from aselective attack of the growing chain on the propene oxide ring. The basis of this assignment is three-fold. Firstly, these structures differ in the number of γ-carbon atoms perceived by the central carbonate carbon atom, being respectively 2, 3, and 4 for the TT, HT, and HH units. Since it is known that γ-carbon atoms make a small negative contribution to the shift of a specific carbon atom, three (groups of) peaks are expected, approximately equally spaced from each other. Secondly, for randomly occurring inversions of propene oxide units in a chain the amounts of head-to-head and tail-to-tail units are statistically equal to each other. The fact that, in the three cases examined, the intensities of the peaks assigned to HH and TT units are indeed equal to each other, is taken as evidence in support of the assignment. The proportion of HT units was 75, 68, and 72%, respectively, for the three sets of reaction conditions;† for completely random propene oxide incorporation this would be 50%. Thirdly, fine structure within each group of peaks, which is considered to arise from as yet undefined tacticity effects, will be the most pronounced in the HH case; consistent with this, the peak assigned as HH shows a greater splitting than that assigned as TT.

The minor peak labelled HT′ is believed to be due to a carbonate carbon atom flanked by more than two propene oxide units. The introduction of one extra unit in an alternating chain creates two such carbonate carbon atoms. The measured ratio of between 1.01 and 1.05 propene oxide : CO_2 units would therefore lead to between 2 and 10% of such carbon atoms. In agreement with this, the intensity of the HT′ peak is *ca.* 5% of the total carbonate carbon resonance.

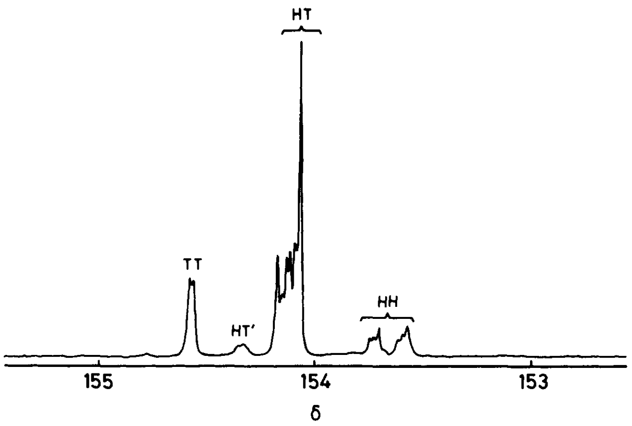

Figure 1. The carbonate carbon atom resonance, obtained at 100 MHz in $CDCl_3$ solution, of a propene oxide–carbon dioxide copolymer prepared (see text) at 55 °C. Polymer concentration in $CDCl_3$ was *ca.* 10% weight; spectrum obtained with a pulse delay of 20 s, and 2700 scans.

The absence of fine structure in the earlier n.m.r. studies could be due to the improved spectral resolution and sensitivity in the present work (spectra obtained at 100 MHz compared to 25 MHz[3] or 20 MHz[4]). Alternatively, details of catalyst preparation, leading to subtle changes in the nature of the active sites, could play a role. This has been suggested to account for varying amounts of HH, HT, and TT units in the polyether obtained from the $Et_2Zn + H_2O$ catalysed homopolymerization of propene oxide.[8]

The propene oxide–carbon dioxide copolymerization probably proceeds *via* an anionic co-ordination mechanism.[1] Our observation of aselective attack on propene oxide is consistent with a Lewis acid (Zn^{2+}) activation of this monomer, which would help to compensate for the weakly nucleophilic character of the monoalkyl carbonate anion.[9]

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† Copolymers were prepared in 1,4-dioxane solution, with the following catalysts, reaction temperatures, and reaction times: $Et_2Zn + H_2O$, 23 °C, 90 h;[5] Et_2Zn + resorcinol, 55 °C, 44 h;[6] Et_2Zn + resorcinol, 35 °C, 48 h.[7]

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