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Mechanisms

Statistics of the formation of ester on syndiotactic methacrylic anhydride-methacrylic acid copolymers

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Summary

The mode of ring opening during methanolysis of syndiotactic methacrylic anhydride-methacrylic acid copolymers has been studied by statistical calculation, Monte Carlo Simulation, and ^{1}H-NMR. Significant deviations from random ring opening are found, indicating that the nature of the monomer unit adjacent to the anhydride ring may exert an influence.

Introduction

Previously, the formation of cyclic anhydride on syndiotactic poly(methacrylic acid) (PMAA) by dicyclohexylcarbodiimide (DCC) has been described (BERG-FELD et al 1981). This reaction yields by nearly random ring formation on the chain a methacrylic anhydride - methacrylic acid (MAH-MAA) copolymer. In the present communication, the MAH-MAA copolymers are fully reacted with methanol to yield by opening of the anhydride ring the corresponding methyl methacrylate - methacrylic acid (MMA-MAA) copolymers. Knowing the statistics of the educt copolymer, the statistics of the ring opening reaction may be investigated. The one-step reaction, i.e. the simultaneous reaction of PMAA with DCC and alcohol (KLESPER et al 1979 a, KLESPER et al 1979 b) or DCC and amine (BERG-FELD and KLESPER 1981) has already been described previously. It is, however, of advantage for the study of the statistics, if the two consecutive reactions are investigated also separately.

Experimental

The MAH-MAA copolymers have been prepared by reacting PMAA with dicylohexylcarbodiimide as described (BERG-FELD et al 1981). However, they were not isolated after their first precipitation in diethylether, but immediately reacted further according to two routes.

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For the determination of the statistics of the MAH-MAA copolymers, the MAA monomer units of the copolymers were fully esterified by diazomethane, followed by hydrolysis of the MAH-units. The statistics of the resulting MMA-MAA copolymers is a replica of the original MAH-MAA copolymers and was determined by ^{1}H-NMR (BERG-FELD et al 1981). The statistics of the MAH-MAA copolymers was not determined directly by NMR because of insufficient spectral resolution. For the study of the mode of ring opening of the MAH-MAA copolymers during esterification, the MAH-MAA copolymers were dissolved in pyridine and reacted with methanol.

The MAH-MAA copolymer, derived from 300 mg (3.5 mmole) PMAA (BERG-FELD et al 1981), was dissolved in 9 ml pyridine at 50 °C and 9 ml methanol and 0.75 ml triethylamine added. After 16 h at 50 °C, the resulting MMA-MAA copolymer was precipitated in 200 ml diethyl ether. It was dissolved in 5 ml 1 N KOH by warming and diluted to 100 ml with water. After reprecipitation at 80 °C - 100 °C using conc. HCl, it was dried at 50 °C in vacuo for at least 12 h. The ^{1}H NMR spectra were recorded in DMSO.d_6 or pyridine. d_5 solution (5 % w/v) at 100 °C, using a Bruker CXP 200 FT spectrometer at 200 MHz and TMS as internal standard. Relative peak areas in the α-CH_3 resonance region were determined by planimeter.

Results and Discussion

It was started from a series of MAH-MAA copolymers of different conversions P(Á). P(Á) is the mole %/100 of Á-monomer units and Á is a methacrylic acid unit within an anhydride ring. The triad statistics of these MAH-MAA copolymers was determined from MMA-MAA copolymers derived by diazomethane methylation and consecutive hydrolytic ring opening (BERG-FELD et al 1981). Only a part of each of the MAH-MAA copolymer, having a given P(Á), was treated in this way, the other part of the MAH-MAA copolymer was reacted with methanol to yield by esterolytic ring opening also MMA-MAA copolymers. The triad statistics of all MMA-MAA copolymers was investigated by ^{1}H-NMR of the α-CH_3 resonance region. Because there exists no serious overlapping of triad peaks in the spectra, all triad probabilities may be determined directly from the spectra (KLESPER et al 1979 a).

For obtaining information about the experimental statistics of the MMA-MAA copolymers obtained by esterolysis with methanol, the statistics was calculated from the known statistics of the MAH-MAA copolymers, assuming thereby random ring opening of the anhydride rings. The term random meaning that there is no statistical influence of the kind of monomer unit neighboring an anhydride ring. For

instance, a methacrylic acid unit does then not lead to an opening of the neighboring anhydride ring in such a way as to introduce a bias toward the formation of two neighboring MAA- units. Instead, there is an equal chance for the opened ring to have the MAA (MMA) unit to the "left" or to the "right".
The calculation of the statistics of the MMA-MAA copolymers was started by correlating to each triad of the MAH-MAA copolymers the triads in the resulting MMA-MAA copolymers, e.g.:

1) $4.0\ \overset{\frown}{AA}\overset{\ulcorner}{A} \rightarrow 1.0\ ABA + 1.0\ ABB + 1.0\ BAA + 1.0\ BAB$

or

2) $4.0\ \overset{\frown}{AA}\overset{\ulcorner}{A}^{+} \rightarrow 1.0\ ABA + 1.0\ ABB^{+} + 1.0\ AAB^{+} + 1.0\ BAB$

Hereby an $\overset{\ulcorner}{A}$ is a MAA-unit bound in an anhydride ring in MAH-MAA copolymers, A a MMA unit in MMA-MAA copolymers, and B a MAA unit in both types of copolymers, while + indicates that the order may be reversed, i.e. $\overset{\frown}{AA}\overset{\ulcorner}{A}^{+}$ contains $\overset{\frown}{AA}\overset{\ulcorner}{A}$ and $\overset{\urcorner}{A}\overset{\frown}{AA}$. Because of reversibility, $\overset{\frown}{AA}\overset{\ulcorner}{A}$ and $\overset{\urcorner}{A}\overset{\frown}{AA}$ are present in equal amounts in the MAH-MAA copolymer chain. Eq. 1 states that of 4.0 triads AAA 1.0 triad of each ABA, ABB, BAA, and BAB are formed as a statistical average during esterolysis. Writing similar equations for all MAH-MAA triads and adding them leads to equations for the triad probabilities $P(X_1X_2X_3)$ of the MMA-MAA copolymers formed by esterolysis

3) $P(AAA) = 0$

4) $P(ABA) = 0.25\ P(\overset{\urcorner}{A}B\overset{\ulcorner}{A}) + 0.25\ P(\overset{\frown}{AA}\overset{\ulcorner}{A}^{+})$

5) $P(AAB^{+}) = 0.25\ P(\overset{\frown}{AA}\overset{\ulcorner}{A}^{+})$

6) $P(ABB^{+}) = 0.50\ P(\overset{\urcorner}{A}BB^{+}) + 0.50\ P(\overset{\frown}{AA}B^{+})$
$+0.50\ P(\overset{\urcorner}{A}B\overset{\ulcorner}{A}) + 0.25\ P(\overset{\frown}{AA}\overset{\ulcorner}{A}^{+})$

7) $P(BAB) = 0.50\ (P(\overset{\frown}{AA}B^{+}) + 0.25\ P(\overset{\frown}{AA}\overset{\ulcorner}{A}^{+})$

8) $P(BBB) = P(BBB)_{MAH-MAA} + 0.50\ P(\overset{\urcorner}{A}BB^{+})$
$+0{,}25\ P(\overset{\urcorner}{A}B\overset{\ulcorner}{A})$

whereby the MAH-MAA triads are in the right hand side of the equations and the MMA-MAA triads on the left. Thus the triad statistics of the MMA-MAA copolymers may be calculated from a known triad statistics of the MAH-MAA copolymers. If the calculation is to be performed in reverse, one may by mutual substitution of eqs. 3 to 8 arrive at:

$$9)\quad P(\overset{\frown}{AA}\acute{A}^{+}) = 4\,P(AAB^{+})$$

$$10)\quad P(\grave{A}B\acute{A}) = 4\,[P(ABA) - P(AAB^{+})]$$

$$11)\quad P(\overset{\frown}{AA}B^{+}) = 2\,[P(BAB) - P(AAB^{+})]$$

$$12)\quad P(\grave{A}BB^{+}) = 2\,[P(ABB^{+}) + 2\,P(AAB^{+}) - P(BAB) - 2\,P(ABA)]$$

$$13)\quad P(BBB)_{MAH-MAA} = P(BBB) - P(ABB^{+}) - P(AAB^{+}) + P(BAB) + P(ABA)$$

Eqs. 9 - 13 require also random ring opening and particular accurate MMA-MAA triad probabilities since the subtractions and the factors in eqs 9 - 13 tend to magnify experimental errors. However, eqs. 1 - 13 are general and apply to other random ring opening reactions in binary copolymers, if the rings are between neighboring monomer units and if two different monomer units are formed by opening a ring.

Eq. 3 is interesting since it states that no triads AAA may be present in the MMA-MAA copolymers. This is true also for nonrandom ring opening reactions and it is in contrast to the reaction in which PMAA is reacted simultaneously with dicylohexylcarbodiimide and alcohol.
The evaluation of the MMA-MAA triads is simple since all six possible triads may be resolved in the ^{1}H- and the ^{13}C-NMR spectra. In Fig. 1 the experimental probabilities of the five triads which may be generated by ring opening are plotted versus the conversion P(A) as points, together with the dashed curves calculated by eqs. 3 - 8. There exist significant deviations between experiment and calculation. In order to support this result of Fig. 1, a Monte Carlo simulation of random ring opening was carried out, starting from a simulated random MAH-MAA copolymer. The simulation yielded the drawn out curves in Fig. 1 which are also deviating from the experimental points by about the same extent. The small differences between the calculated and simulated curves are due to the fact that the simulation started from a MAH-MAA copolymer of random ring closure while these copolymers have in fact a small tendency toward alternation between anhydride rings and methacrylic acid units (BERG-FELD et al 1981).

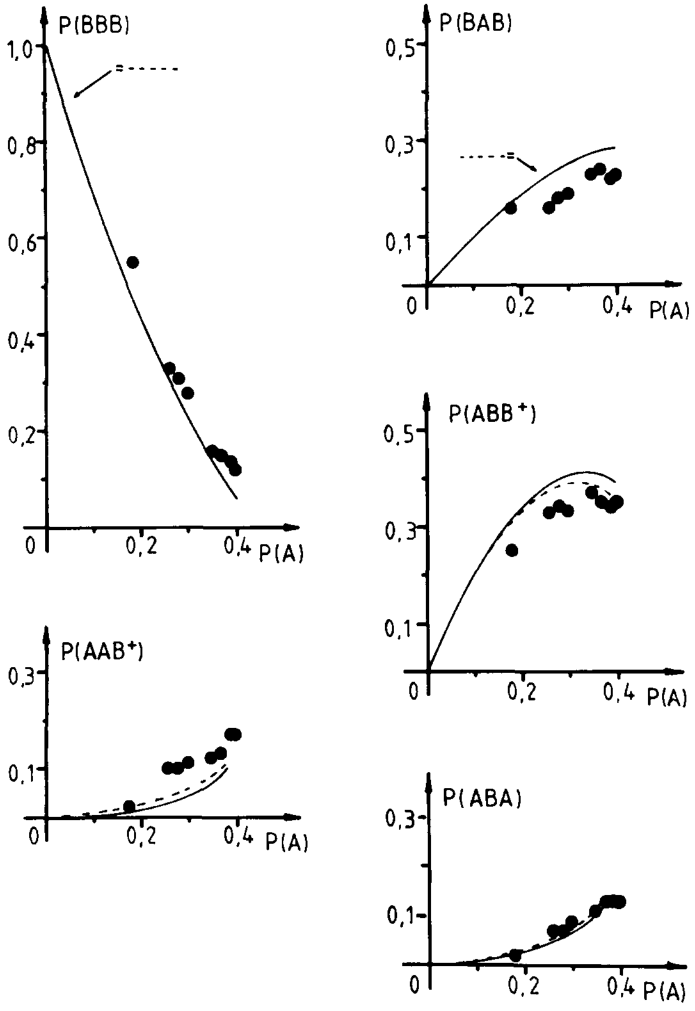

Fig. 1 The experimental probabilities of the five triads present in MMA-MAA copolymers obtained by methanolysis of MAH-MAA copolymers [o]. The probabilities calculated by eqs. 3 - 8 are given for comparison [----], as well as the probabilities obtained by Monte-Carlo simulation [———].

Inspection of the deviations in Fig. 1 shows that there are more AA, less AB$^+$, and about the expected amount of BB when compared to calculation. This can be derived from the generally valid equations

14) $P(AA) = 0.5\ P(AAB^+) + P(AAA)$

15) $P(AB^+) = 2\ P(ABA) + P(ABB^+)$

16) $P(BB) = 0.5\ P(ABB^+) + P(BBB)$

An excess of AA and a deficiency in AB$^+$ could mean that a given A-unit adjacent to a ring $\overset{\frown}{AA}$ would bias the ring opening in favor of formation of an A next to a given A. That is, an esterified unit favors the formation of an adjacent esterified unit.

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