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Formation of Cyclic Anhydride on Syndiotactic Poly(methacrylic Acid) by Cyclohexylcarbodiimide

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Summary

The reaction of syndiotactic poly(methacrylic acid)(s-PMAA)with cyclohexylcarbodiimide, in the absence of alcohols,amines, or other compounds reactive with anhydride, leads to methacrylic anhydride(cyclic)-methacrylic acid (MAH-MAA) copolymers. For determining the statistics of these soluble linear copolymers, a complete esterification of the methacrylic acid monomer units by diazomethane is carried out, the anhydride ring not being affected by the diazomethane. By a consecutive hydrolysis step, the anhydride is cleaved, resulting in methyl methacrylate - methacrylic acid (MMA-MAA) copolymers whose statistics is a replica of the original MAH-MAA copolymers and which can be easily determined by NMR.The statistics of the copolymers is not Bernoullian with respect to the distribution of the dimethacrylic acid anhydride rings and the methacrylic acid units, but the ring forming reaction is nearly random along the chain with a small tendency toward alternation for MAH-rings and MAA-units.

Introduction

It has been demonstrated that the esterification and amidation of syndiotactic poly(methacrylic acid)(s-PMAA) in the presence of dicyclohexylcarbodiimide (DCC) takes place via a sixmembered dimethacrylic acid anhydride ring as a necessary intermediate (KLESPER et al 1979 a,b; BERG-FELD and KLESPER 1982). The esters and amides form only by consecutive reaction of the cyclic anhydride. Here, the reaction of s-PMAA with DCC alone,in the absence of alcohol or amine,is studied. The statistics of the resulting MAH-MAA copolymers is evaluated by consecutive esterification of the MAA-units by diazomethane to methyl methacrylate units, followed by the hydrolysis of the MAH-rings to MAA-units. The triad statistics of the final methyl methacrylate-methacrylic acid (MMA-MAA) copolymers is analogous to the original MAH-MAA copolymers and has the advantage of being more easily determined by ^{1}H-NMR.

In Fig. 1 the sequence of the polymer analogous reactions on the original MAH-MAA copolymers is shown on a triad as a chain segment, together with a scheme of the concurrent transformations of triads.For obtaining a MMA-MAA copolymer which is a replica of the precursor MAH-MAA copolymer, complete reactions are necessary. While this is easily achieved for the hydrolysis, care must be exercised for the esterification which can be carried out with diazomethane in anhydrous DMSO and BF_3 as a catalyst. Moreover, premature hydrolysis before completion of the

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esterification must be avoided since this alters the conversion and may also alter the triad statistics. The resolution of the ^1H NMR spectra at 200 MHz is sufficient for deciding on detail on features of the statistics (KLESPER et al. 1975)

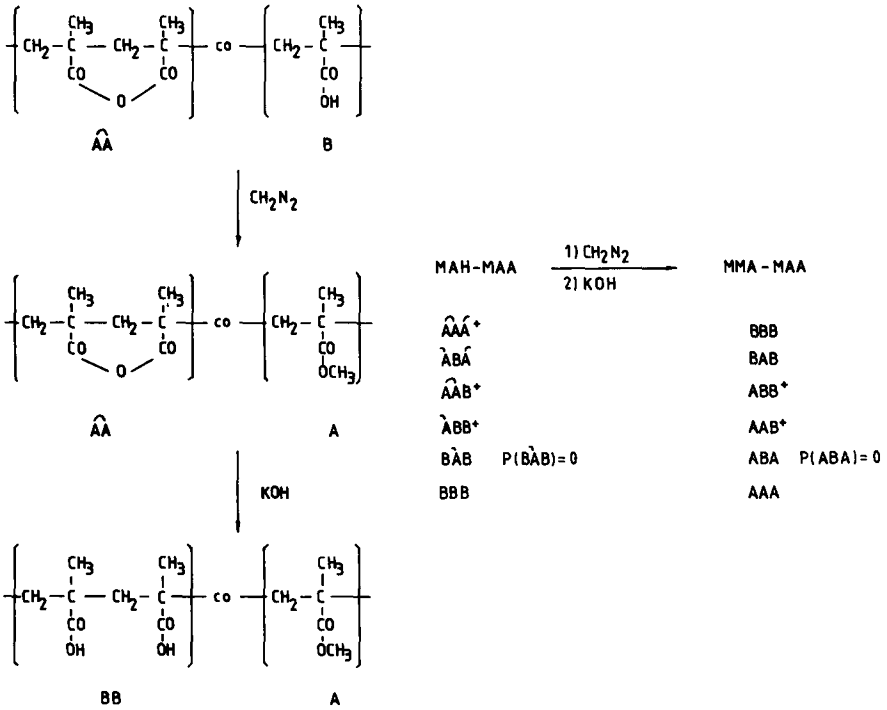

Fig. 1 Reactions on syndiotactic methacrylic anhydride-methacrylic acid (MAH-MAA) copolymers to yield syndiotactic methylmethacrylate-methacrylic acid (MMA-MAA) copolymers, together with a listing for the transformation of triads (A = MMA-unit; Á = half of methacrylic anhydride ring; A͡A = methacrylic anhydride ring; B = MAA-unit)

Experimental

The s-PMAA was prepared as described before (KLESPER et al 1979a). Preparation of MAH-MAA copolymers: To 300mg (3.5 mmole) s-PMAA dissolved in 9 ml pyridine was added 720 mg (3.5 mmole) DCC in 3 ml pyridine and 0.75 ml triethylamine. Occasionally up to 1 ml of H_2O was added to aid in dissolving the s-PMAA in pyridine. After a given reaction time at 50°C, it was stopped by precipitating the polymer in 200 ml dry diethylether. Representative reaction times were: 10 min, P(Á)= 0,54; 15 min. P(Á)= 0.60; 30 min. P(Á) = 0.68; 60 min. P(Á) = 0.74; 90 min. P(Á) = 0.80 (Á ≙ half an anhydride ring). After filtering, the precipitated polymer was redissolved in 10 ml dry DMSO with warming. On slow cooling, the dicyclohexylurea cristallizes and can be removed by filtration. The copolymer is precipitated in 500 ml dry ether and dried in vacuo at 50°C. In Fig. 2 an IR-spectrum of s-PMAA (trace I) is compared with that of a MAH-MAA copolymer of $P(\acute{A}) = 0.76$ (trace II). A characteristic strong double absorption band of υ >C = O at 1820 (weaker) and 1775 cm^{-1} (stronger) points to cyclic anhydride, another strong band at 1030cm^{-1} indicates C-O-C in anhydride. The presence of linear anhydride can also be excluded because of the solubility of the polymer. Omitting triethylamine, however, may lead to insoluble, crosslinked polymers.

Esterification of the MAH-MAA copolymers: For the esterification of the MAH-MAA copolymers by diazomethane to MAH-MMA copolymers and the subsequent hydrolysis to MMA-MAA copolymers, the same procedure is followed for the preparation of the MAH-MAA copolymers. However, after the first precipitation by diethylether, the urea is not removed by crystallization from DMSO. Instead, the ether precipitate is suspended in DMSO at room temperature and a threefold excess of a CH_2N_2 solution in DMSO added (calculated on all monomer units), followed by 1 ml $(C_2H_5)_2O\cdot BF_3$ as a catalyst. N_2-evolution is rapid and subsides after 15 minutes. After 2 h of stirring, the urea is filtered off. The polymer is precipitated in ether, redissolved in 1 N KOH, thereby hydrolysing simultaneously all anhydride rings, and filtered. The solution is diluted with H_2O to 200 ml, heated to 80°C and precipitated with conc. HCl. The conditions suffice also to completely esterify s-PMAA. Furthermore, complete esterification is indicated by the absence of ABA triads in the MMA-MAA copolymers, because this triad can only be formed by incomplete methylation.

Recording of spectra: The ^1H-NMR spectra were obtained with a Bruker CXP-200 FT-spectrometer operating at 200 MHz. The solutions (5% w/v) were measured at 100°C using TMS as internal standard. Relative peak areas were determined by planimeter. The IR-spectra were recorded on a Perkin-Elmer IR-spectrometer 283 using the KBr press technique.

Results and discussion

According to FLORY(1939), the limiting conversion for cyclizations, involving immediately adjacent monomer units, is 86.5%, assuming a random ring formation along the chain. Somewhat smaller maximum values of 80% are found in the present case, which is compatible with an also observed small tendency toward alternation. The experimental probabilities of the triads $P(\overparen{AA}\acute{A}^{+}) = P(\overparen{AA}\acute{A}) + P(\grave{A}\overparen{AA})$, $P(\grave{A}B\acute{A})$, $P(\overparen{AA}B^{+}) = P(\overparen{AA}B) + P(B\overparen{AA})$, $P(\grave{A}BB^{+}) = P(\grave{A}BB) + P(BB\acute{A})$, and $P(BBB)$ are given in table 1. Also given is $P(\acute{A})$ according to $P(\acute{A}) = P(\overparen{AA}\acute{A}^{+}) + P(\overparen{AA}B^{+})$. The probabilities have been obtained by ^1H-NMR of the MMA-MAA copolymers derived from the MAH-MAA copolymers.

Copolymers of a type as obtained by cyclization of adjacent monomer units are necessarily of a non-Bernoullian statistics. This can be immediately seen in the limit of conversion, because then only single uncyclized monomer units are allowed between cyclized rings and not two or more uncyclized units. However, it is of interest to determine how large the deviation is at conversions considerable below the limiting conversion. For Bernoullian statistics it must, for instance, hold

1) $P'(\overparen{AA}\overparen{AA}) = \left[P'(\overparen{AA})\right]^2$

Table 1

Comparison of experimental triad probabilities with calculated Bernoullian triad probabilities. Calculated values in parenthesis below experimental probabilities

$P(\overset{\rceil}{A})$	$P(\overset{\frown}{AA}\overset{\lceil}{A}^{+})$	$P(\overset{\rceil}{A}B\overset{\lceil}{A})$	$P(\overset{\frown}{AA}B^{+})$	$P(\overset{\rceil}{A}BB^{+})$	$P(BBB)$
0.18	0.00 (0.02)	0.02 (0.01)	0.18 (0.16)	0.15 (0.15)	0.65 (0.67)
0.27	0.02 (0.04)	0.02 (0.02)	0.25 (0.22)	0.22 (0.18)	0.50 (0.52)
0.34	0.03 (0.07)	0.05 (0.03)	0.31 (0.27)	0.24 (0.22)	0.37 (0.42)
0.58	0.14 (0.24)	0.10 (0.07)	0.44 (0.34)	0.22 (0.20)	0.10 (0.15)
0.66	0.24 (0.33)	0.13 (0.08)	0.42 (0.33)	0.16 (0.17)	0.04 (0.09)
0.72	0.31 (0.41)	0.15 (0.09)	0.41 (0.32)	0.14 (0.14)	0.00 (0.05)
0.72	0.34 (0.41)	0.13 (0.09)	0.38 (0.32)	0.14 (0.14)	0.00 (0.05)
0.75	0.37 (0.45)	0.14 (0.09)	0.38 (0.30)	0.12 (0.12)	0.00 (0.04)
0.76	0.38 (0.47)	0.14 (0.09)	0.38 (0.29)	0.10 (0.12)	0.00 (0.04)
0.76	0.42 (0.47)	0.14 (0.09)	0.34 (0.29)	0.10 (0.12)	0.00 (0.04)

The P'( ) are probabilities normalized to the sum of the monads $\overset{\frown}{AA}$ and B, e.g.

$$2)\quad P'(\overset{\frown}{AA}) = \frac{N(\overset{\frown}{AA})}{N(\overset{\frown}{AA}) + N(B)} = \frac{N(\overset{\frown}{AA})}{\frac{N(\overset{\rceil}{A})}{2} + N(B)}$$

N = number

$\overset{\frown}{AA}$= anhydride ring

$\overset{\rceil}{A}$ = half an anhydride ring

B = MAA-unit

For converting the P'( ) to "normal" probabilities P( ), which are normalized to the monads A and B, the enumerator and denominator in eq. 2 may be divided by $[N(\overset{\rceil}{A}) + N(B)]$, leading to

$$3)\quad P'(\overset{\frown}{AA}) = \frac{P(\overset{\frown}{AA})}{\frac{(P(\overset{\rceil}{A})}{2} + P(B)}$$

In a similar way

$$4)\quad P'(\overset{\frown}{AA}\overset{\frown}{AA}) = \frac{P(\overset{\frown}{AA}\overset{\frown}{AA})}{\frac{P(\overset{\rceil}{A})}{2} + P(B)}$$

Substitution of eqs.3 and 4 in eq. 1 yields

$$5)\quad \frac{[P(\overset{\frown}{AA})]^2}{\left[\frac{P(\overset{\rceil}{A})}{2} + P(B)\right]^2} = \frac{P(\overset{\frown}{AA}\overset{\frown}{AA})}{\frac{P(\overset{\rceil}{A})}{2} + P(B)}$$

In consideration of

$$6)\quad P(\overset{\frown}{AA}\overset{\frown}{AA}) = P(\overset{\frown}{AA}\acute{A}) = P(\overset{\frown}{AA}\acute{A}^{+})/2$$

and

$$7)\quad P(\overset{\frown}{AA}) = \frac{P(\acute{A})}{2}$$

one obtains from eq. 5

$$8)\quad P(\overset{\frown}{AA}\acute{A}^{+}) = \frac{2\left[\frac{P(\acute{A})}{2}\right]^{2}}{\frac{P(\acute{A})}{2} + P(B)}$$

as the equation for the triad $\overset{\frown}{AA}\acute{A}^{+}$. The transformation of the P'( ) to the P( ) is necessary, because only the latter probabilities can be directly determined by NMR. Eqs. 9 to 12 give the expressions for the other triads which are possible in copolymers obtained by cyclization of neighboring monomer units.

$$9)\quad P(\grave{A}B\acute{A}) = \frac{P(B)\cdot\left[\frac{P(\acute{A})}{2}\right]^{2}}{\left[P(B) + \frac{P(\acute{A})}{2}\right]^{2}}$$

$$10)\quad P(\overset{\frown}{AA}B^{+}) = \frac{P(B)\cdot P(\acute{A})}{P(B) + \frac{P(\acute{A})}{2}}$$

$$11)\quad P(\grave{A}BB^{+}) = \frac{\left[P(B)\right]^{2}\cdot P(\acute{A})}{\left[P(B) + \frac{P(\acute{A})}{2}\right]^{2}}$$

$$12)\quad P(BBB) = \frac{\left[P(B)\right]^{3}}{\left[P(B) + \frac{P(\acute{A})}{2}\right]^{2}}$$

Thus probabilities of all triads may be calculated for a Bernoullian distribution of the events $\overset{\frown}{AA}$ and B in the chain. The calculated values are also given in Table 1 (in parenthesis). There are less triads $\overset{\frown}{AA}\acute{A}^{+}$ and BBB and more triads $\grave{A}B\acute{A}$ and $\overset{\frown}{AA}B^{+}$ experimentally found at higher conversion than are calculated. At lower conversions such discrepancies cannot be expected to have developed. The triad $\grave{A}BB^{+}$ shows the least deviation. In all, the deviations from Bernoullian statistics are considerable. Rings immediately adjacent to each other are apparently disfavored in the copolymers, while rings separated by one B-unit occur more often than demanded by Bernoullian statistics. While the statistics of $\overset{\frown}{AA}$ and B is and cannot be Bernoullian, the ring closure along the chain might still be random, as can be tested by a Monte Carlo Simulation of the reaction. In Fig.3 the experimental triad probabilities of the MAH-MAA copolymers (points) are compared with a Monte Carlo Simulation of random ring closure (broken curve). Apparently, there are also fewer triads $\overset{\frown}{AA}\acute{A}^{+}$ and BBB and more triads $\grave{A}B\acute{A}$ and $\overset{\frown}{AA}B^{+}$ formed in the actual copolymers than corresponds to a random ring closure. The discrepancies are smaller than in the comparison with the Bernoullian statistics, but appear still to be significant. Changing the Monte-Carlo Simulation to one in which the ring

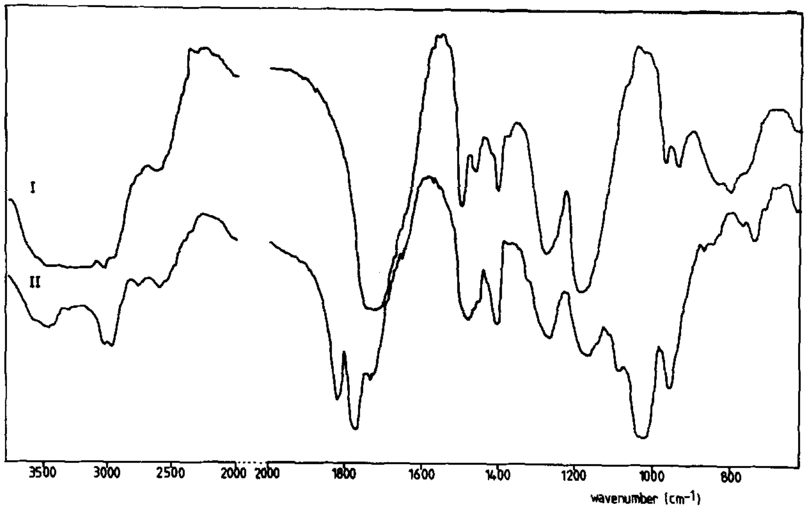

Fig.2 IR-spectra of syndiotactic poly(methacrylic acid) (trace I) and a MAH-MAA copolymer of P(Á)= 0.76 (trace II)

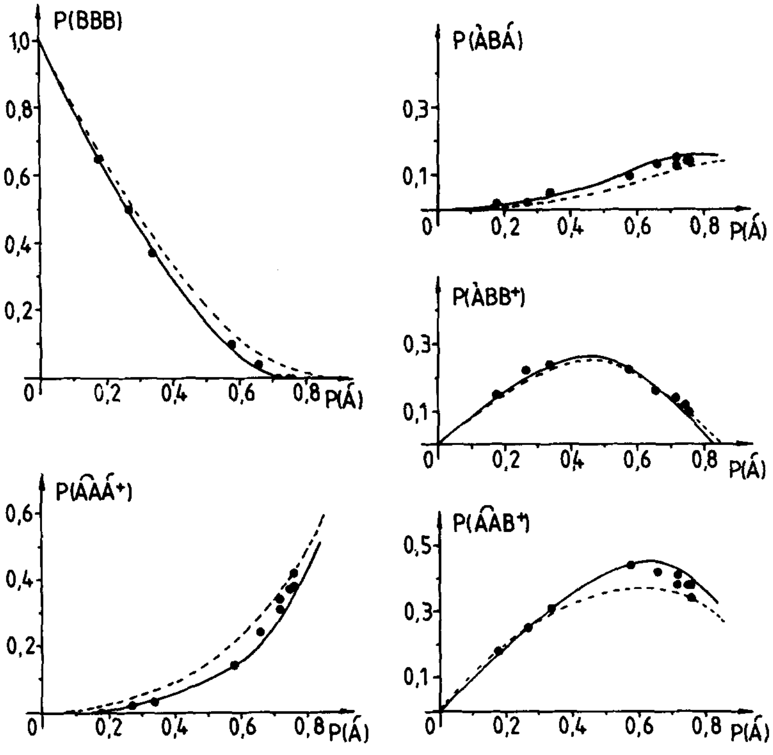

Fig. 3 Triad probabilities of MAH-MAA copolymers. Experimental probabilities(points),probabilities obtained by random ring closure in a Monte Carlo Simulation (----), and those obtained by a Simulation with neighboring group effect (———)

closure is not entirely random, more specifically to one with a lesser ring closure speed for B-units near rings, leads to the fully drawn out curve in Fig. 3. The experimental points are found between the two types of curves, indicating that the real ring closure follows intermediate kinetic parameters.
The Monte Carlo Simulations were carried out with end to end connected chains of a total of 4000 monomer units. The monomer units were called successively by random numbers. Ring closure took place whenever another random number fell within a preset range. In Fig. 4 the ranges for the Monte Carlo Simulations of Fig. 3 are given. For the random ring closure in (a) there

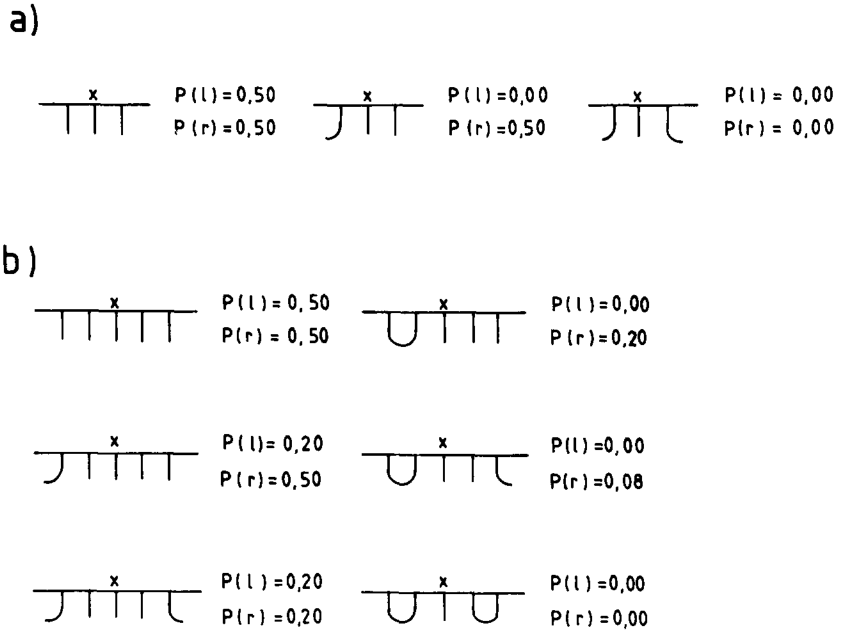

Fig. 4 Reaction probabilities in the Monte Carlo Simulation with (a) random ring closure, and (b) with neighboring group effect. The reaction probabilities are given for ring closure to the left, P(l), of the called monomer unit (x) and to the right, P(r). They represent the range within which a random number leads to ring closure. T = MAA-unit, U= anhydride ring

exists no neighboring group effect, except that no ring can be formed where already one is present. P(1) = 0.5 means, for instance, that all random numbers from 0 to 0.5 lead to ring formation to the left of the called monomer unit, whereby the called monomer unit is marked (x). The ring closure with a kinetic neighboring group effect in (b) follows a more diversified set of ranges, but is otherwise analogous. The set of ranges is chosen as to disfavor kinetically the formation of a ring immediately adjacent to another ring already present. At least three ranges will have to be set for (b) independently. The ranges chosen here are characterized by 0.50, 0.20 and 0.08. Assuming, for instance, that a random number has called the sequence characterized by P(l) = 0.20 and P(r) = 0.50, then the ranges for this sequence are set as 0 to 0.20 for ring closure to the left and 0.20 t0 0.70 for ring closure to the right. If the newly generated random number falls in none of the two ranges, but within 0.70 t0 1.00, no ring is being formed.

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