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^{1}H-NMR of the Amidation of Syndiotactic Poly(Methacrylic Acid) with Carbodiimide

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Summary

The reaction of syndiotactic poly(methacrylic acid) with dicyclohexylcarbodiimide in the presence of benzylamine yields syndiotactic methacrylic acid-methacryloyl-N-benzylamide copolymers. A limiting conversion to amide of about 62% and a tendency of alternation for the monomer units is observed by ^{1}H-NMR. The amidation is accompanied by the formation of a smaller amount of cyclic imide as a side reaction. The imide portion can also be transformed into amide by a consecutive hydrolysis step.

Introduction

The amidation and esterification of acids by means of carbodiimides, particularly dicyclohexylcarbodiimide (DCC) is well known for the synthesis of peptides (GREENSTEIN and WINITZ,1961) and oligonucleotides (KHORANA,1961) but has been lacking in its application to synthetic polymers, e.g. to polymers processing acid-, hydroxyl-, or amine groups in each monomer unit. Previously, we have investigated the esterification of syndiotactic poly(methacrylic acid)(s-PMAA) with low molecular weight alcohols in the presence of DCC(KLESPER and STRASILLA,1977; KLESPER et al, 1979 a,b), resulting in syndiotactic methacrylic acid-methacrylic ester copolymers with at most 62% conversion and a tendency for alternation of the monomer units. Both the limiting conversion and the alternation is the result of cyclic anhydride as an intermediate product. In this communication, the application of DCC to the amidation of polymethacrylic acid with benzyl amine and the determination of the statistics of the resulting copolymers by ^{1}H-NMR is reported.

Experimental

For amidation, a solution of 720 mg DCC (3,5 mmole) in 3 ml pyridine was added to 300 mg s-PMAA(3,5 mmole) in 9 ml pyridine and kept at 50°C. Consecutively, the desired amount of a stock solution of 2 g benzyl amine in 100 ml pyridine was added over a period of 10-20 min. After an additional reaction time of 2 h at 50°C, the amidation was stopped by precipitating with 100 ml ether. The precipitate was filtered and redissolved in 10 ml DMSO at 80°C. By slow cooling the dicyclohexylurea cytallizes. After filtering off the urea, the copolymer is again precipitated in 100 ml ether. The ether is decanted and the copolymer redissolved in 10 ml pyridine. Final precipitation is in 100 ml H_2O, adding a small amount of conc. HCl , as required. The co-

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polymer is dried at 50°C in vacuo for at least 12 h.

Using a molar ratio of 1:1:1 for s-PMAA, DCC and benzyl amine, the conversion is about 62% after 2 h. Copolymers of lower conversion are prepared in 2 h reaction time by reducing the amount of benzyl amine. To hydrolyze the imide rings, the copolymer is dissolved in 10 ml 1 N aqueous KOH and refluxed for 2 h. The solution is diluted to 100 ml and precipitated by dropwise addition of conc. HCl, as required.

^{1}H-NMR spectra were taken on a Bruker CXP-200 spectrometer at 200 MHz, 100°C and TMS as internal standard. Peak areas were measured by planimeter. IR-spectra were recorded on a Perkin-Elmer spectrometer 283 B by the KBr technique.

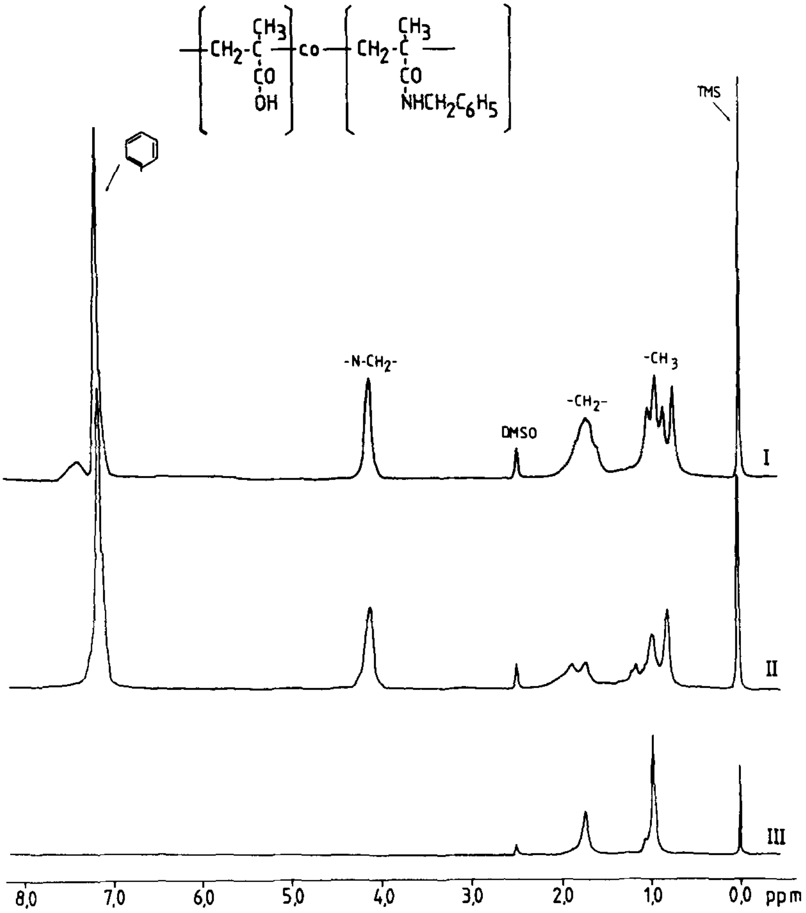

Fig. 1 ^{1}H-NMR spectra of a syndiotactic methacrylic acid-methacryloyl-N-benzyl amide copolymer (trace I), an atactic poly(methacryloyl-N-benzyl amide) (trace II), and syndiotactic poly(methacrylic acid) (trace III)

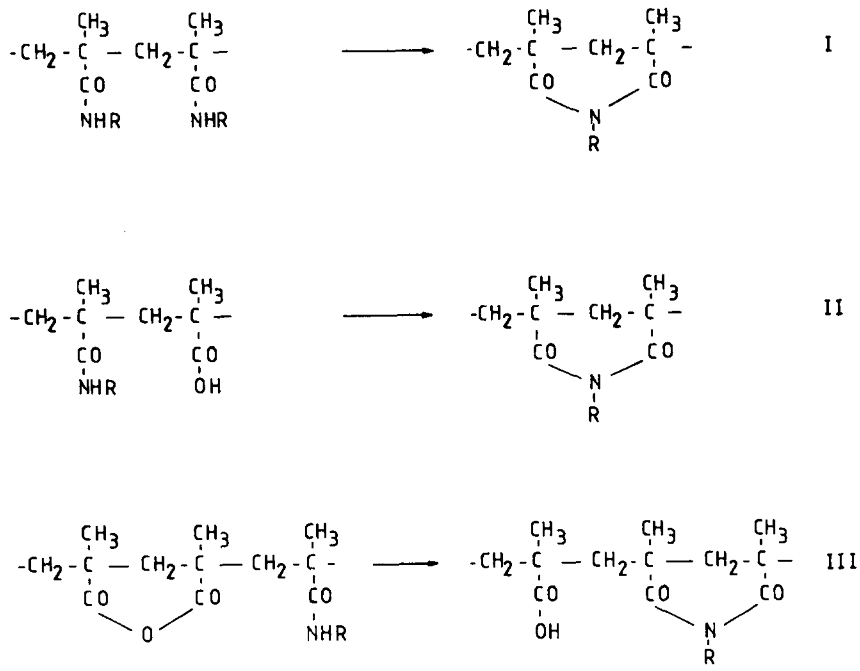

Fig. 2 Possible reactions I, II, and III, leading to sixmembered cyclic imide on a methacrylate polymer chain

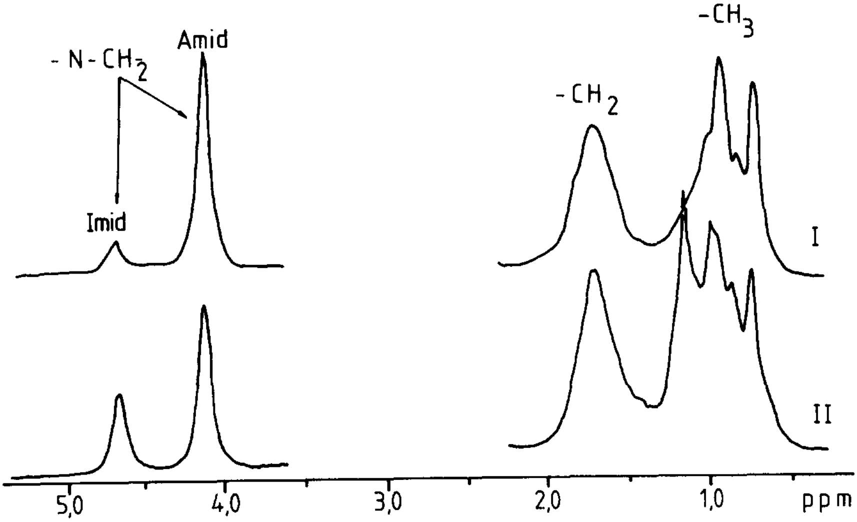

Fig. 3 Partial ^{1}H-NMR spectra of a methacrylic acid-methacryloyl-N-benzyl amide copolymer,before (trace I), and after heat treatment in quinoline (trace II)

Results and Discussion

In Fig. 1 the ^1H-NMR spectra of a methacrylic acid-methacryloyl-N-benzyl amide copolymer (MAA-MABA)(spectral trace I), the atactic poly(methacryloyl-N-benzyl amide)(PMABA) prepared by radical polymerization of the corresponding monomer (trace II), and of s-PMAA (trace III) are seen. The MAA-MABA copolymer contains no imide rings. The α-CH_3 resonance of the MAA-MABA copolymer is reasonably well resolved, showing the effect of compositional syndiotactic triads. The PMABA shows configurational triads in the α-CH_3 region, most likely in the order s, h, i, whereby only the syndiotactic peak A_SA_SA at highest field is of interest here. Comparison of traces II and III with trace I points to A_SA_SA and B_SB_SB (A=amide, B=acid) being in the second and third peak of the MAA-MABA copolymers, counting from high to low field.

In the IR-spectra, bands at 1720 and 1660 cm^{-1} correspond to carboxylic acid and carbonamide, respectively.The amide II band (ν N-H) is seen at 1510 cm^{-1}. The absorptions of the aromatic ring are located at 3080, 3060 and 3025 cm^{-1} for ν C-H,750 cm^{-1} for σ C-H, 1080 cm^{-1} for monosubstituted aromatic rings.The conversion was determined as P(A) by the relative areas (I) of the peaks in the ^1H NMR spectra, according to

$$1)\quad P(A) = \frac{I_{arom.}}{I_{\beta\text{-}CH_2\text{-}} + I_{\alpha\text{-}CH_3}} = \frac{5\, I_{\text{-}NCH_2\text{-}}}{2(I_{\beta\text{-}CH_2} + I_{\alpha\text{-}CH_3})}$$

The determination of the P(A) from the area of the aromatic resonance, $I_{arom.}$, yielded, however, values of P(A) which were in agreement with those from I_{-NCH_2-} only when both the larger peak at 4,1 ppm and the smaller peak at 4,7 ppm were considered as $-NCH_2-$ resonances.(See Fig. 3 for peaks at 4.1 and 4.7 ppm)It was therefore assumed that the peak at 4.1 ppm stems from amide ($-NHCH_2$Ø) and the one at 4.7 ppm from cyclic imide ($>NCH_2$Ø),the latter being formed by a side reaction.

Several authors have observed the formation of cyclic imide during the polymerization of methacryloyl amide (CRAUWELS and SMETS,1950) and the thermolysis(HAAS and MACDONALD,1971) or hydrolysis (MOENS and SMETS, 1957) of unsubstituted poly(methacryloyl amide). In view of these findings and the known formation of anhydride from s-PMAA and DCC alone(KLESPER et al,1979 a,b), the possibilities I to III of Fig.2 may be considered for the formation of cyclic imide during the present reaction.According to I, the imide is formed from an amide diad. This possibility could be excluded by heating a DMSO solution of atactic PMABA to 170°C and observing an unchanged spectrum for the PMABA. Using the same conditions, or a quinoline solution at 170°C, for the MAA-MABA copolymers, an imide formation according the possibility II was in fact observed. This can be seen in Fig. 3 by the change in the relative intensity of the two peaks at 4.1 and 4.7 ppm in the $-NCH_2-$ region. Spectral trace II represents the copolymer after being heated at 170°C for 2 h. In addition, the imide formation greatly changes the relative intensities in the α-CH_3 resonance which emphasizes that this region in the presence of imide cannot be used to evaluate sequences in terms of a binary MAA-MABA copolymer. If the temperature of heat treatment is lowered from 170° to 100°

no imide formation is observed after several hours. This indicates that reaction possibility II is also not followed during the amidation reaction at 50°C. There remains reaction possibility III, based on cyclic anhydride adjacent to an amide monomer unit. The intermediate presence of cyclic anhydride on the chain can be postulated, because the same reaction mechanism appears to prevail for the amidation as for the esterification of s-PMAA with DCC. This conclusion may be drawn from the same limiting conversion (62%) and the same statistics over the range of conversion (see Fig.6). Thus anhydride and amide are simultaneously present on the chain, leading as is well known for low molecular weight compounds, to imide.

For obtaining a truly binary acid-amide copolymer without imide, the imide often being present in an amount between 10 and 25% of total $-NCH_2-$, the imide must be hydrolized later to amide. By an aftertreatment of the copolymer in refluxing aqueous 1 N KOH, the imide $-NCH_2-$ resonance disappears and the amide $-NCH_2-$peak increases correspondingly, i.e. there is no noticeable change in P(A). By the aftertreatment, any anhydride which may be still present at this time is also reconverted to acid, as is desirable. It should be noted that the higher the imide content is, the more of a small change in statistics is to be expected when compared to the statistics of an acid-amide copolymer which has been formed without imide from the start.

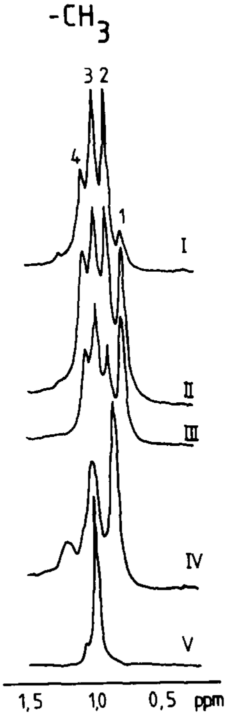

Fig.4 Partial ^{1}H-NMR spectra of the α-CH_3 group in methacrylic acid-methacryloyl-N-benzyl amide copolymers containing no imide. Amide content increasing from trace I to III(P(A)=0.28; 0.52; 0.62). Atactic poly(methacryloyl-N-benzyl amide) shown in trace IV and syndiotactic poly(methacrylic acid) in trace V.

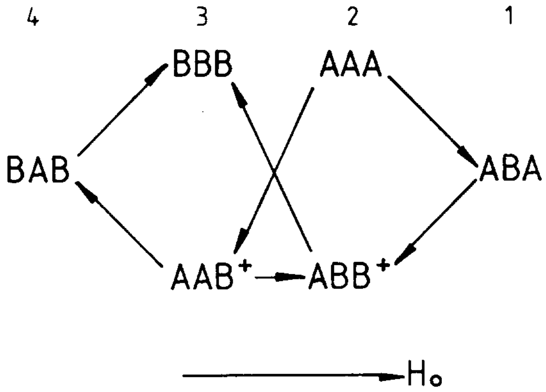

Fig. 5 Triad assignment of the α-CH_3 resonance in the MAA-MABA copolymers. Peak positions numbered 1 to 4. The direction of the arrows indicates substitution of A by B.

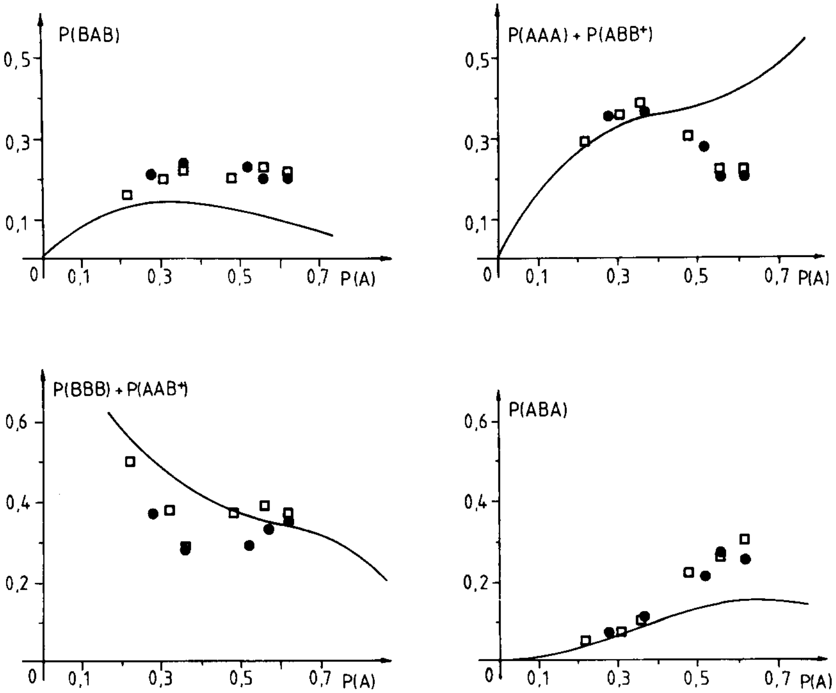

Fig. 6 Triad probabilities of copolymers resulting from amidation [●] and from esterification [□] of syndiotactic poly(methacrylic acid) by benzyl amine or methanol, respectively. The curves are calculated for Bernoullian statistics.

The α-CH_3 resonance region of aftertreated MAA-MABA copolymers is shown in Fig. 4. Extra shoulders and peaks due to imide have disappeared. For the assignment of 6 triads to 4 observable peaks it was considered that the known assignment of A_SA_SA and B_SB_SB is consistent with the postulated shift rules of Fig.5. According to this assignment, substitution of a central A by a B leads to a shift of one position to higher field and substitution of a flanking A by B to a shift of one position downfield. The assignment may be supported by comparison of the peak intensities for amidation with the peak intensities for esterification of PMAA by methanol and DCC in Fig.6(KLESPER et al,1979 a).The ^1H-spectra of the methacrylic acid-methyl methacrylate copolymers are resolved into all 6 triads which for the comparison in Fig. 6 have been partly added in pairs. The agreement between amidation[●] and esterification[○] suffices for supporting the assignment. However, an exact correspondence in statistics between amidation and esterification cannot be expected because the velocity of anhydride cleavage by amin and alcohol is different.

The comparison of the experimental points of BAB and ABA with the calculated Bernoullian curves in Fig. 6 clearly shows a tendency for alternation of the monomer units not only for esterification, but also for amidation.

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