Polymer Bulletin 2, 691–698 (1980)

Polymer Bulletin

NMR of the Formation of Cyclic Imide on Poly(Methacrylic Acid)

K. Ziegenberg and E. Klesper

Lehrstuhl für Makromolekulare Chemie der Technischen Hochschule Aachen,
5100 Aachen, Federal Republic of Germany

Summary

The reaction of syndiotactic poly(methacrylic acid) and formamide above 100°C yields a syndiotactic copolymer of methacrylic acid and dimethacryloylimide. The ^{13}C-NMR spectra of the copolymers show resolved α-CH_3 and >C=0 resonances which are evaluated to yield the triad probabilities. The triad statistics prove a nearly random formation of the cyclic imide along the polymer chain.

Introduction

Several authors observed the formation of cyclic imides starting from poly(vinylamides). STAUDINGER and URECH (1929), CRAUWELS and SMETS (1950), BRESLER et al (1960), and HAAS and MACDONALD (1971) found imide ring formation with thermal treatment of poly(vinylamides). Also, by acid catalyzed hydrolysis of poly(vinylamides) (MOENS and SMETS(1957)), or the aminolysis of poly(methylmethacrylate) at 240° (SCHRÖDER (1961), BAUMANN et al(1960)) the formation of dimethacryloyl imide units was found. In addition, the imide was found to be already formed when vinyl amide was polymerized (CRAUWELS and SMETS(1950) HAAS and MACDONALD(1971)). In general, the nitrogen content and IR were employed to demonstrate presence and amount of imide rings. The methods were, however, not entirely sufficient for a quantitative analysis of conversion, and did not yield the relative frequency of sequences.

In the present report, syndiotactic methacrylic acid-dimethacryloylimide (MAA-MAI) copolymers of different composition were prepared by the reaction of syndiotactic poly(methacrylic acid) (s-PMAA) with formamide (FA) and investigated by NMR-spectroscopy. When s-PMAA is heated with formamide above 100°C one obtains copolymers whose imide ring content increases with increasing reaction time and which are no longer soluble in water or methanol. A similar reaction could be carried out in N-methylformamide but not with dimethylformamide. Apparently an amidation takes place by the formamides, which is followed by a ring closure to imide. The reaction path in Figure 1 is considered possible because the copolymers often contain a small amount of amide besides a larger quantity of cyclic imide.

0170-0839/80/0002/0691/$01.60

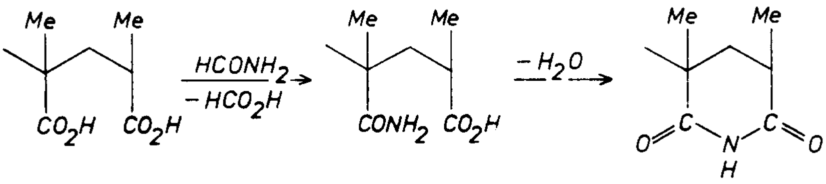

Fig. 1 Path of amide and imide formation in the reaction of s-PMAA with FA

Results and Discussion

In the NMR-spectra of tactic binary copolymers six triads are to be expected if reversed forms cannot be differentiated. In case of the methacrylic acid - dimethacryloylimide copolymers, however , the triad AIA (A=methacrylic acid unit, I=methacryloyl unit participating in an imide ring) cannot exist because an imide ring possesses two consecutive units I. Of the remaining five triads the sequences $\overset{+}{\mathrm{IAA}}$ (IAA and AAI) and AAA should disappear when the reaction is nearing completion. Figure 2 shows the ^{13}C-NMR spectra of MAA-MAI copolymers with reaction time, i.e. conversion,increasing from spectral traces I to IV. Both the α-CH_3 and the >C=0 carbons are usefully resolved, whereby the assignments proposed in Figure 2 are identical but in opposite order. The assigments are based on the two arguments mentioned , the position of AAA in PMAA(trace I), the expectation of a systematic assignment with the approximate validity of shift rules and the observation that equ. 1 and 2 are obeyed: Hereby

$$P(AI) = P(IA) \qquad (1)$$

was actually used in the form of

$$P(\overset{+}{IIA})/2 - P(IAI) - P(\overset{+}{IAA})/2 = 0 \qquad (2)$$

For the left hand side of equ. 2 there resulted for 21 copolymers over the range of conversion, together with standard deviation,

$$\alpha - CH_3 \text{ region} : 0.004 \pm 0.013$$

$$>C = 0 \quad \text{region} : -0.012 \pm 0.013$$

It was ascertained moreover by inverse gated decoupling that the relative peak areas within a given resonance region are not noticeable influenced by the NOE. Chemical shifts over the range of conversion are given in Table 1. The conversion is obtained by averaging between

$$P(I) = P(III) + P(\overset{+}{IIA}) \qquad (3)$$

and

$$P(I) = P(III) + P(\overset{+}{IIA})/_2 + P(IAI) + P(\overset{+}{IAA})/_2 \qquad (4)$$

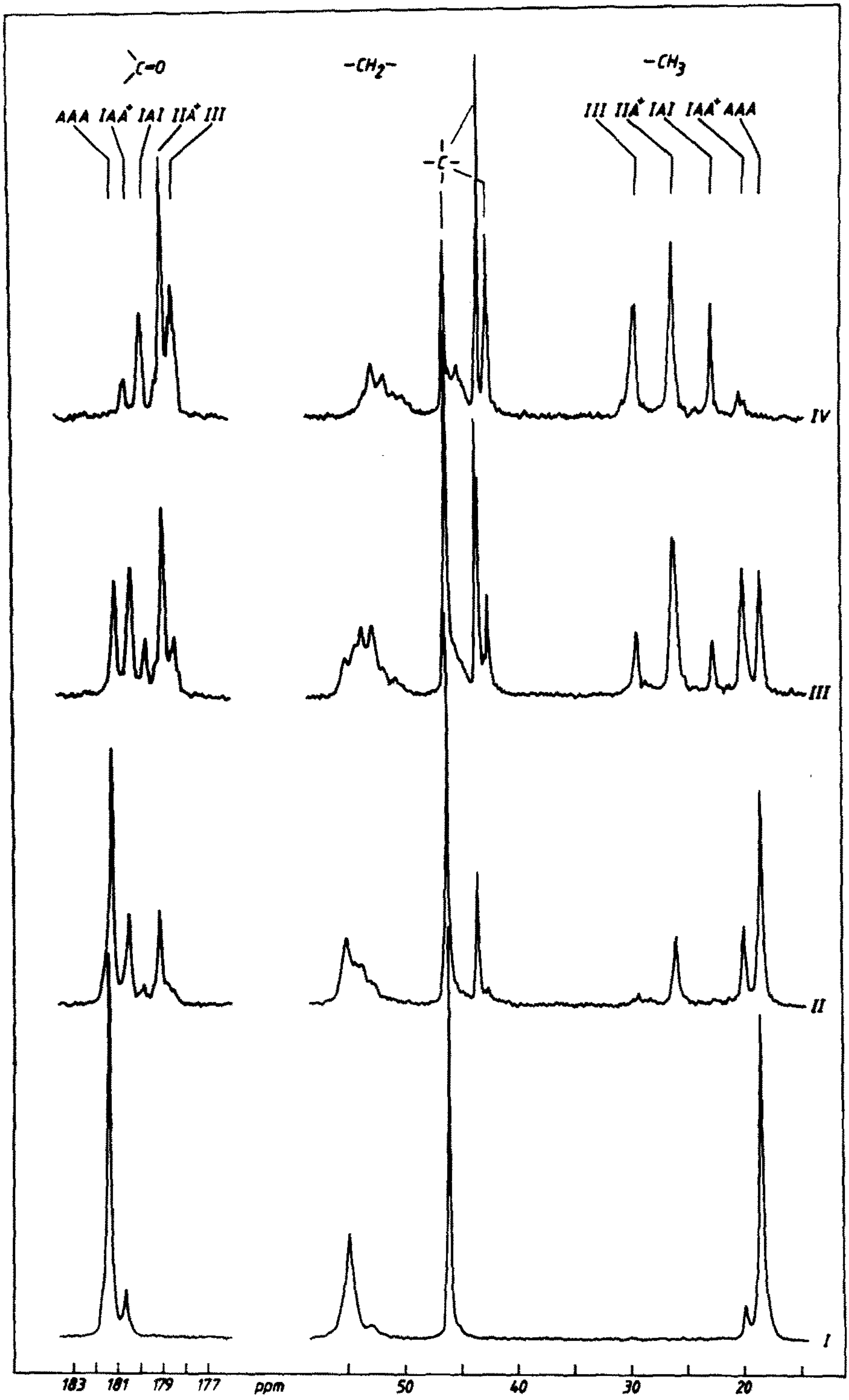

Fig.2 Expanded ^{13}C-NMR spectra of syndiotactic PMAA (trace I) and MAA-MAI copolymers of different conversion; trace II, P(I) = 0.25; trace III, P(I) = 0.48; trace IV, P(I) = 0.74. Solvent: Pyridine d_5 with 10% water, 85°C

TABLE I

triad	chem. shift (ppm)	
	>C = 0	α-CH_3
III	178.5 - 178.7	29.2 - 29.5
IIA$^+$	179.0 - 179.3	25.7 - 26.1
IAI	179.8 - 180.1	22.5 - 22.6
IAA$^+$	180.4 - 180.8	19.7 - 20.1
AAA	181.2 - 181.6	18.2 - 18.4

syndiotactic and heterotactic triads of PMAA (s = syndiotactic, i = isotactic)

A_sA_sA	181.5	18.5
$A_sA_iA^+$	180.8	19.9

The triad probabilities for the α-CH_3 and >C = 0 resonances agree within ± 0.015 while the conversions, P(I), agree within about ± 0.020.

In Figure 3 the ^{1}H-NMR spectrum of the copolymer of trace III of Figure 2 is shown. The resolution of the α-CH_3 resonance at 90MHz is unsatisfactory. However,a broad resonance appears at about 10 ppm which is attributed to the >NH proton of the imide rings. An additional smaller peak at 6.7 ppm is due to an impurity, probably the -NH_2 protons of the -CH_2-C(CH_3)($CONH_2$)- monomer unit which is present in all copolymers in varying amounts. The intensity of the peak could be reduced to some extent by subsequent heating of the copolymers at 180°C in DMSO, at the same time increasing the imide content. One apparently observes a ring closure of amide to imide. Quantitative evaluation resulted in amide monomer unit content of up to 7 mole % in different copolymers. The amide content is probably the reason for the valleys not to reach the base line entirely in the α-CH_3 region of the ^{13}C-NMR spectra.

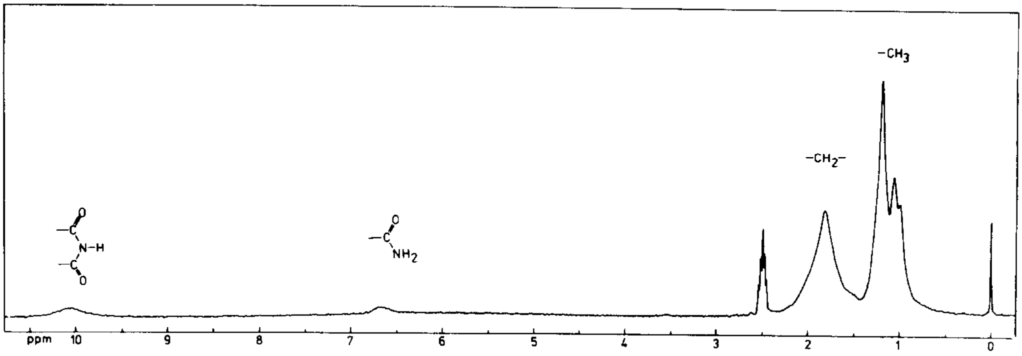

Fig.3 ^{1}H-NMR-spectrum of a$_o$MAA-MAI copolymer of P(I)= 0.48. Solvent DMSO.d$_6$, 90 C

In Table 2 analytical data of six copolymers are compared. The conversion P(I) of column A has been obtained from both the α-CH_3 and the $>C=0$ resonance of the ^{13}C-NMR spectra. The probability of amide monomer units (mole %/100) in column B is extracted from the ^{1}H-NMR spectra. The elemental analysis gives rise to the average number of nitrogen atoms for all monomer units in column C. Finally, in column D it is calculated by the entries in columns A and B what is to be expected in column C.

TABLE 2

copolymer	A P(I)	B P(-$CONH_2$)	C x in C_4N_x	D= A/2 + B
1.	0.430	0.051	0.290	0.266
2.	0.480	0.044	0.314	0.284
3.	0.605	0.061	0.375	0.364
4.	0.625	0.061	0.399	0.374
5.	0.745	0.032	0.408	0.405
6.	0.805	0.010	0.417	0.413

If all nitrogen would be present in form of the imide, then A = 2C. This is only fullfilled with the highest conversions (copolymer 6). Usually, A <2C, which points to the presence of other forms of nitrogen besides imide. Considering the presence of amide in addition, then A + 2B = 2C, or A/2 + B = C. This relation is reasonably well fullfilled with different conversions, but less so with lower conversions. Thus it cannot be excluded that still another form of nitrogen is present in minor amounts.

The statistics of imide rings along the chain has been determined by following the triad probabilities over the range of conversion. FLORY (1939) has calculated the limiting conversion as 0.865 $(1 - 1/e^2)$ assuming a random ring formation between neighboring monomer units without any kinetic neighboring group effect. For some reactions this limiting conversion has been found experimentally, e.g. in case of the reaction of PVC with Zn. In case of the imide ring formation, however, starting from polyacryl- or polymethacrylamides, this limit could not be reached (HAAS and MACDONALD (1971)). By following the triad probabilities it is possible to determine at each conversion whether the ring closure is random or not. This determines in turn the limiting conversion. For a statistics having a tendency for alternation this limit is necessarily lower, while for a blocklike statistics it must be higher than Flory's value.

In Figure 4 the experimental probabilities of 4 triads are shown over the range of conversion (points). Also shown are the results of a Monte Carlo simulation, together with their standard deviations (hatched areas). The simulation was based on the assumption of a random ring closure, i.e. on the absence of a kinetic

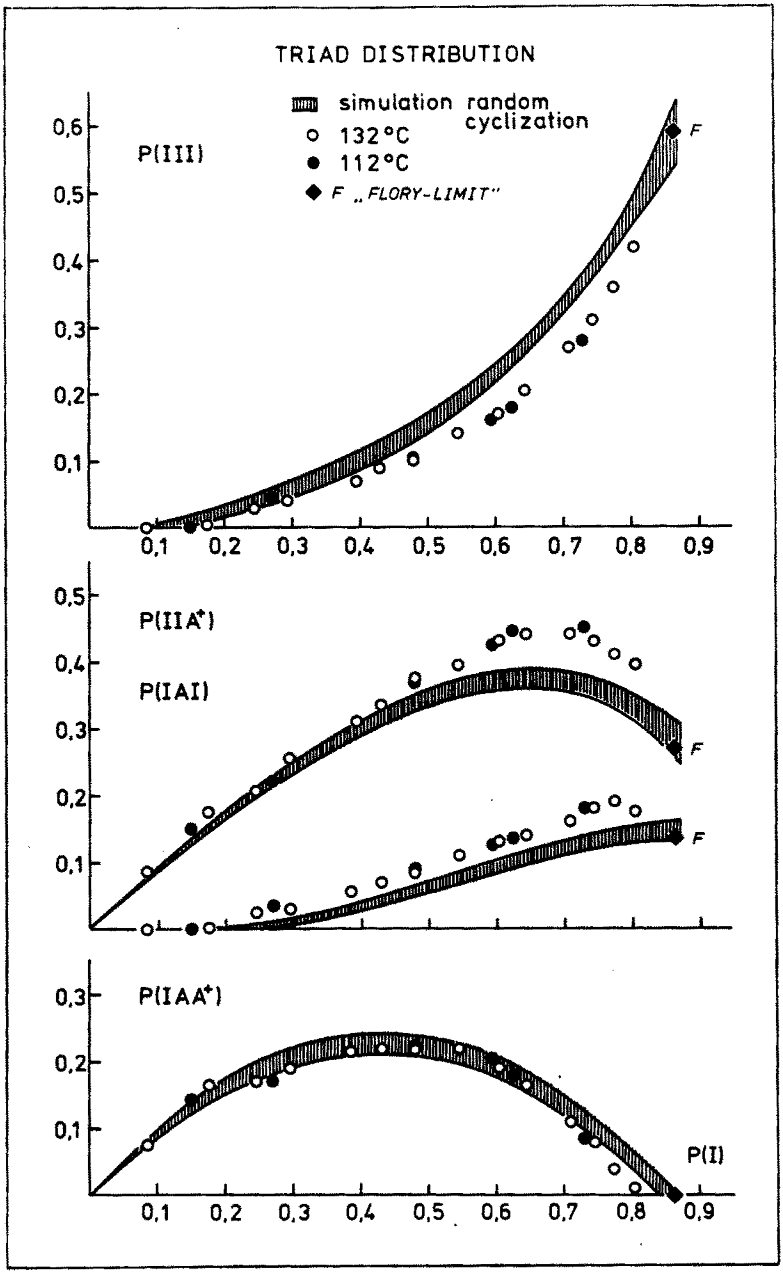

Fig. 4 Triad statistics during formation of MAA - MAI copolymers. Eyperimental data with two reaction temperatures shown as points, Monte Carlo simulation of random cyclization given as hatched areas.

neighboring group effect. The simulation coincides with the triad probabilities calculated for the limiting conversion starting from (P(AIA)= $1/e^2$ = 0.135. This leads to P(AII$^+$) = 0.270 and together with (P(AAA) = 0 and P(AAI$^+$) = 0 one obtains P(III) = 1 - 0.135 - 0.270 = 0.595. The imide ring formation occurs in fact nearly random with a small tendency toward alternation. With respect to this tendency it is not unlikely that the separation of the rigid imide ring by one MAA-unit is conformationally favored in the transition state over adjacent imide rings. At P(I) = 0.81 all triads IAA$^+$ have already disappeared and no ring closure is possible any more. The reaction must then stop at this limiting conversion.

Experimental

Syndiotactic PMAA was prepared according to KLESPER et al (1979). For the preparation of syndiotactic MAA-MAI copolymers, 1 g PMAA was dissolved in 27 ml freshly distilled formamide at 60°C and kept under N_2 for specified periods at 112° or 132°C. After cooling and precipitation in acetone it was filtered and briefly dried in vacuo. The polymer was then dissolved in 100 ml 0,05 KOH, diluted to 500 ml with water, and reprecipitated by dropwise adding concentrated HCL. It was heated to 80°C and filtered. After drying in vacuum copolymers are obtained which are soluble in DMSO,DMF,pyridine or dioxane,the latter two containing small amounts of water. The copolymers are insoluble in H_2O, methanol, $CHCl_3$ or benzene. Figure 5 shows the conversion with time at a reaction temperature of 132°C.

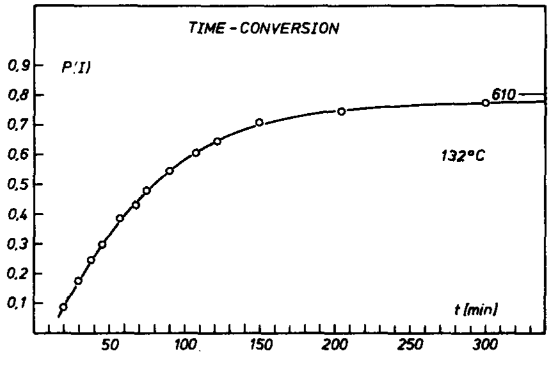

Fig.5 Conversion with time at 132°C for the preparation of MAA-MAI copolymers

The MAA-MAI copolymers may be hydrolyzed by 5 n KOH. By refluxing at ambient pressure the P(I) decreases from 0.8 to 0.3 within 3 h. At 120°C in a closed ampoule the P(I) decreases from 0.8 to 0.03, i.e. to nearly pure PMAA in 20h.With the conditions of reprecipitation employed, no noticeable hydrolysis was found.

NMR spectra were recorded on a Bruker WH-90 multinuclear FT-NMR instrument with TMS as internal standard and a concentration of 10-20% polymer. The peak areas in the NMR spectra were determined by planimeter. For the ^{13}C-NMR spectra of the α-CH_3 group the areas between peaks were neglected. From the area of AAI^+ 8% of AAA was subtracted since $A_sA_iA^+$ amounts to 8% of A_sA_sA in PMAA and because $A_sA_iA^+$ coincides with AAI^+. Other heterotactic triads were disregarded because they are probably distributed over the α-CH_3 resonance and their assignment is not known.

The Monte Carlo simulation was carried out on runs of 244 monomer units each in form of a macrocycle. The standard deviation of 5 runs is reproduced in Figure 4. Pseudo random numbers were generated by the equation $x_{i+1} = (ax_i + c) \bmod m$ ($a = 24298$, $c = 99991$, $m = 199017$).

Acknowledgement

The work was supported by the Deutsche Forschungsgemeinschaft by financial aid to one of us (K.Z.) and by granting a NMR-FT-spectrometer to the Institut für Makromolekulare Chemie der Universität Freiburg where all NMR measurements were performed.

References

BAUMANN, U., SCHREIBER, H., SCHRÖDER, G. and TESSMAR, K.: Angew. Chem. 72, 274 (1960)

BRESLER, S.E., KOTON, M.M., OS'MINSKAIA, A.T., POPOV, A.G. and SAVITSKAIA, M.N.: Polymer Sci. USSR (Engl.Transl.) 1,393 (1960)

CRAUWELS, K. and SMETS, G.:Bull.Soc.Chim.Belges, 59,182(1950)

FLORY, P.J.: J.Amer.Chem.Soc.,61, 1518 (1939)

HAAS, N.C. and MACDONALD, R.L.: J. Polym.Sci., A-1,9.3,3583(1971)

KLESPER, E., STRASILLA, D. and BERG, M.C.: European Polymer J., 15, 587 (1979)

MOENS, J. and SMETS, G.: J. Polym.Sci., 23, 931 (1957)

SCHRÖDER, G. : Angew. Chem., 73 , 245 (1961)

STAUDINGER, H. and URECH, F.: Helv.Chim. Acta, 12, 1107 (1929)

Received May 7/ Accepted May 9, 198o