Stereochemical Configuration of Poly(maleic acid) as Studied by ^{13}C NMR

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Received April 11, 1997; Revised Manuscript Received July 9, 1997[⊗]

ABSTRACT: The tacticity of poly(maleic acid) has been resolved by 150-MHz ^{13}C NMR spectroscopy in 0.1 N HCl solution at 60 °C by using the chemical shifts from the backbone carbon atoms and the carboxyl carbon atoms. The racemic propagation is found to be preferred by a factor 2 over mesomeric propagation. The resonances of the carboxyl carbon atoms can be assigned to configurations of heptad sequences along the polymer chain.

Introduction

Poly(maleic acid) (PMA) differs from common polyacids, like poly(acrylic acid) (PAA) and poly(methacrylic acid), by twice as large a density of acid groups along the polymer chain. This larger density manifests itself in the dissociation behavior of PMA. If a homogeneously charged line or rod were an adequate model, the titration behavior of PMA up to 50% neutralization should be identical to that of PAA up to full charge. Furthermore the titration curves of PMA and poly(fumaric acid) (PFA), its stereoisomer, should be identical. Both predictions are found to be wrong. Up to 50% charge PMA is found to be a stronger acid than PAA is. At a neutralization of 50% PMA shows a clear step in p*K*, which PFA does not.[1]

Kawaguchi et al. investigated the dissociation behavior of PMA and PFA by potentiometric titration and infrared spectroscopy.[1−3] Using the Ising model they carried out a calculation for the dissociation behavior. The known configuration of PFA[4] and an assumed configuration of PMA were included in this model to account for the positioning toward each other and the distance between the acid groups which influence intramolecular interactions like charge interactions and hydrogen bonding between acid groups. They obtained no quantitative agreement between model calculation and experimental data. However, qualitatively the difference in dissociation behavior between PMA and PFA could be explained. The infrared measurements on PFA were also interpreted by using the known tacticity of PFA, while the behavior of PMA was explained by hydrogen bonding between neighboring carboxyl groups connected by racemic (r) bonds. An obvious difference between PFA and PMA is that in PFA every other bond has the mesomeric (m) configuration, while in PMA every other bond is r, forcing pairs of acid groups close together. In PFA the chain will then only consist of isolated acid groups and pairs of acid groups while in PMA no isolated acid groups will be present but only stretches of one or more pairs. These stretches that just consist of racemic bonds will create isotactic parts in the polymer chain over which hydrogen bonds and charges can be stabilized because of the regular structure and short distance between carboxylates. Pairs of neighboring acid groups also occur in PIM (poly(maleic acid-*co*-isobutene)). The differences in dissociation behavior between PMA and PIM were explained by the fact that in PIM the pairs alternate with isobutene, while in PMA every backbone carbon carries a carboxylic acid group. Obviously the extent of intramolecular hydrogen bonding and the electrostatic interaction will be determined by the tacticity of the polyelectrolytes.

The tacticity of PFA was determined by Wang et al.[4] This polyacid is prepared by radical polymerization of fumarate esters and it is found that the ratio of racemic to mesomeric propagation is determined by the size of the ester groups. The bulkier the alkyl group, the more r propagation is favored over m propagation. PMA, however, cannot be prepared in this way. Instead it is made by radiation-induced polymerization of maleic anhydride followed by hydrolysis. The polymerization mechanism is unknown, therefore no predictions on the tacticity can be made.

The purpose of this work is to determine the tacticity of nonalkylated PMA dissolved in hydrochloric acid with ^{13}C NMR. In this way the tacticity of the pure polyacid is obtained and the results can be applied directly to measurements performed with the same PMA. The measurements we perform to investigate the behavior of PMA upon charging are potentiometry and infrared spectroscopy. To clear up the total electrostatic surrounding of PMA, NMR counterion relaxation rates and transport properties of counter and polyions by pulsed field gradient NMR have been determined. Transport and dimensional properties of PMA have also been studied by viscometry and light scattering. Papers on these subjects are in preparation.

Experimental Section

Preparation of PMA was done as described by Lang et al.[5] About 88 g of purified maleic anhydride dissolved in 134 g of purified acetic anhydride was sealed under vacuum in a round 200 mL vial. Both purifications consisted of distillation of the compounds (A. R. grade) through a predried 50-cm column. The main fractions were directly collected in the vial. The solution was degassed by freeze thawing several times under vacuum followed by flame sealing of the vial. Polymerization was done at room temperature by irradiating the vial with 1.75 kGray/h ^{60}Co γ rays for 71 h at the Interfacultair Reactor Instituut (IRI) of Delft University of Technology, The Netherlands. The polymer was first diluted by adding 100 mL of butanone. This solution was dripped into 2 L of toluene were the polymer precipitated. The precipitate was filtered and washed with toluene. After drying the precipitate it was converted to PMA by hydrolysis in 0.1 N HCl for 3 weeks. PMA was purified by dialysis against water. Hydrolysis and dialysis were both performed at 4 °C.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

S0024-9297(97)00495-6 CCC: $14.00

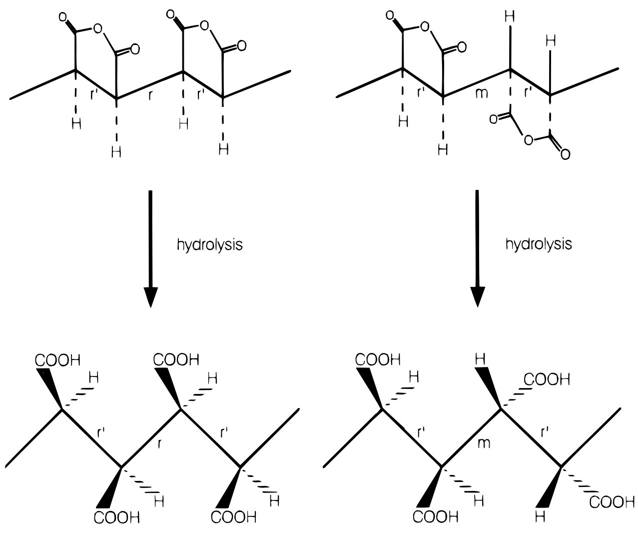

Figure 1. (Left) Development of a racemic propagation during syntheses of PMA. (Right) Development of a mesomeric propagation during syntheses of PMA.

The molecular weight distribution was studied with gel permeation chromatography (GPC) using multi-angle laser light scattering (MALLS) with a DAWN DSP-F detector. The GPC/MALLS measurements were carried out on a Waters model 150C HPLC chromatograph with a TSK gel G5000-G3000 PW column of 60 cm from Toyo Soda Company. A 0.5 M $NaNO_3$ solution was used as the eluent. For the calculation of the molar mass distribution the value of $\delta n/\delta c$ ($\lambda = 633$ nm, at 25 °C) was determined with a differential refractometer at 0.144 ± 0.002 mL/g.

The obtained M_w of PMA is 17600 ± 300, which means that the average polymer consists of 152 monomer units and 303 bonds in the backbone. The M_w/M_n ratio is determined at 1.5 after correcting M_n by comparing with dextrans with a known M_n in the same order of magnitude.[6]

PMA was dissolved in 0.1 N HCl to oppose autodissociation. Autodissociation would cause a shift of about 4.7 ppm for the carboxyl carbon and 3.5 ppm for the backbone carbon[7,8] and complicates the interpretation of the ^{13}C spectrum.

Concentration of the sample was 223 g of PMA/kg of 0.1 N HCl. The ^{13}C spectrum of the sample in a 5-mm tube was recorded on a Bruker DMX-600 spectrometer at 60 °C.

Results and Discussion

The stereochemical configuration of PMA during polymerization is determined by the propagation of the maleic anhydride monomers to poly(maleic anhydride). The mechanism of this polymerization is unknown. But the low M_w and the high energy required to initiate the polymerization indicate that propagation occurs very slowly.[9] In Figure 1 the two possible propagations of the monomers in poly(maleic anhydride) are shown. The propagations can be either racemic (r) or mesomeric (m) and their probabilities are respectively P_r and $P_m = 1 - P_r$.

By hydrolysis of the monomer units racemic bonds inside the maleic acid monomer units are formed. Therefore, every other bond in PMA is a racemic bond denoted as r′.

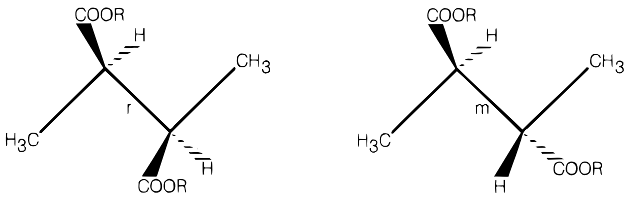

Figure 2. Model compounds for PMA; *rac*- and *meso*-di-(*R*)-2,3-dimethylsuccinate.

Therefore every carbon is directly surrounded by an r′ bond and an r or m bond. This neighborhood of the carbons influences their chemical shifts in the ^{13}C NMR spectra. How these r and m bonds influence the chemical shifts can be determined by comparison with chemical shifts of model compounds for PMA. The shifts for these model compounds (Figure 2), racemic and mesomeric di-(*R*)-2,3-dimethylsuccinate, are given in Table 1. Independent of the kind of alkylation or solvent the presence of a racemic bond in the vicinity shifts the "backbone" carbon about 1 ppm less and the carboxyl carbon about 0.5 ppm more than the presence of a mesomeric bond.

In Figures 3 and 4 the ^{13}C NMR spectra of the PMA backbone carbon atom and carboxyl carbon atom respectively are shown. For both kinds of carbon atoms it is obvious that there are two groups of resonances. However, this is most evident for the carboxyl carbon atom spectra where these groups are completely separated. The existence of the two groups is a result of differences in the direct surroundings of the carbon atoms. As mentioned before, in the case of model compounds, the $\underline{\mathrm{r'r}}$ triad will shift the carboxyl carbon more and the backbone carbon atom less then the $\underline{\mathrm{r'm}}$ triad. Because the $\underline{\mathrm{r'r}}$ triad is the result of a racemic propagation step, the integrals of the groups with the highest carboxyl carbon shift and the lowest backbone carbon shift are a measure for the probability of racemic propagation, P_r. This value of P_r is 0.655 ± 0.015 when determined by integrating the two carboxyl carbon groups. The value of P_r determined from the integrals of the backbone carbon groups are about the same but with a much lower accuracy.

In each of the two carboxyl groups four resonances can be discerned. Figure 5 illustrates how these eight resonances can be assigned to heptad sequences on the polymer chain. It shows that the r or r′ bonds in the triads directly situated next to the observed carbon, underlined in Figure 5 and Table 2, shift the carboxyl carbon the most. Additional r bonds in the vicinity of the triad shift the carbon some more. The resonances of the backbone carbons are not so clear as those of the carboxyl carbons. Nevertheless the group with the lowest shift looks like the mirror image of the carboxyl carbon resonances, as expected.

In Table 2 calculated probabilities of triad and heptad sequences are given. Assuming statistically indepen-

Table 1. Chemical Shifts of PMA Model Compounds; *rac*- and *meso*-Di-(*R*)-2,3-dimethylsuccinate

model compds for m and r bonds in PMA	chemical shift "backbone" C, ppm	chemical shift carboxyl C, ppm	frequency, MHz	solvent
meso-diisopropyl 2,3-dimethylsuccinate[4]	43.89	175.1	125	$CDCl_3$
rac-diisopropyl 2,3-dimethylsuccinate[4]	42.91	175.7	125	$CDCl_3$
meso-dimethyl 2,3-dimethylsuccinate[10]	42.6	175.0	50	Dioxan
rac-dimethyl 2,3-dimethylsuccinate[10]	41.7	175.5	50	Dioxan
meso-2,3-dimethylsuccinic acid[11]	42.05	175.84	15	$CDCl_3$
rac-2,3-dimethylsuccinic acid[11]	41.03	176.50	15	$CDCl_3$

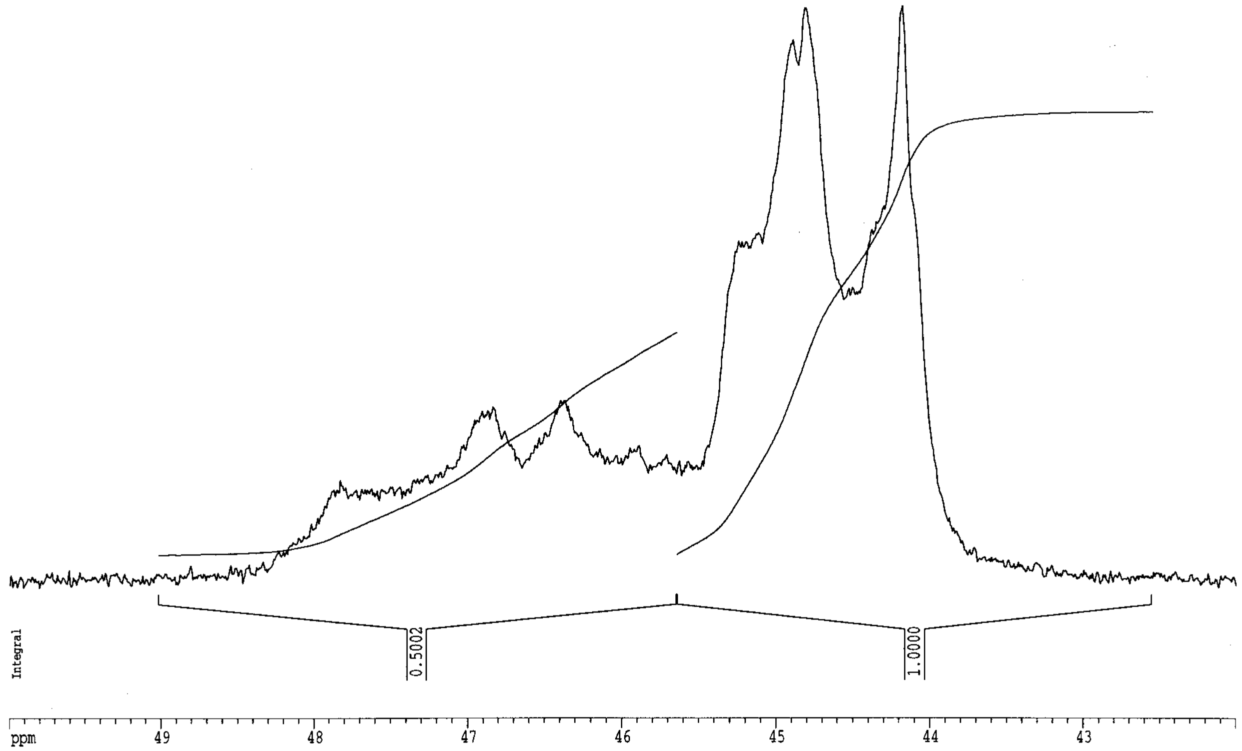

Figure 3. ^{13}C NMR spectrum of the PMA backbone carbon in 0.1 N HCl at 60 °C and 150 MHz.

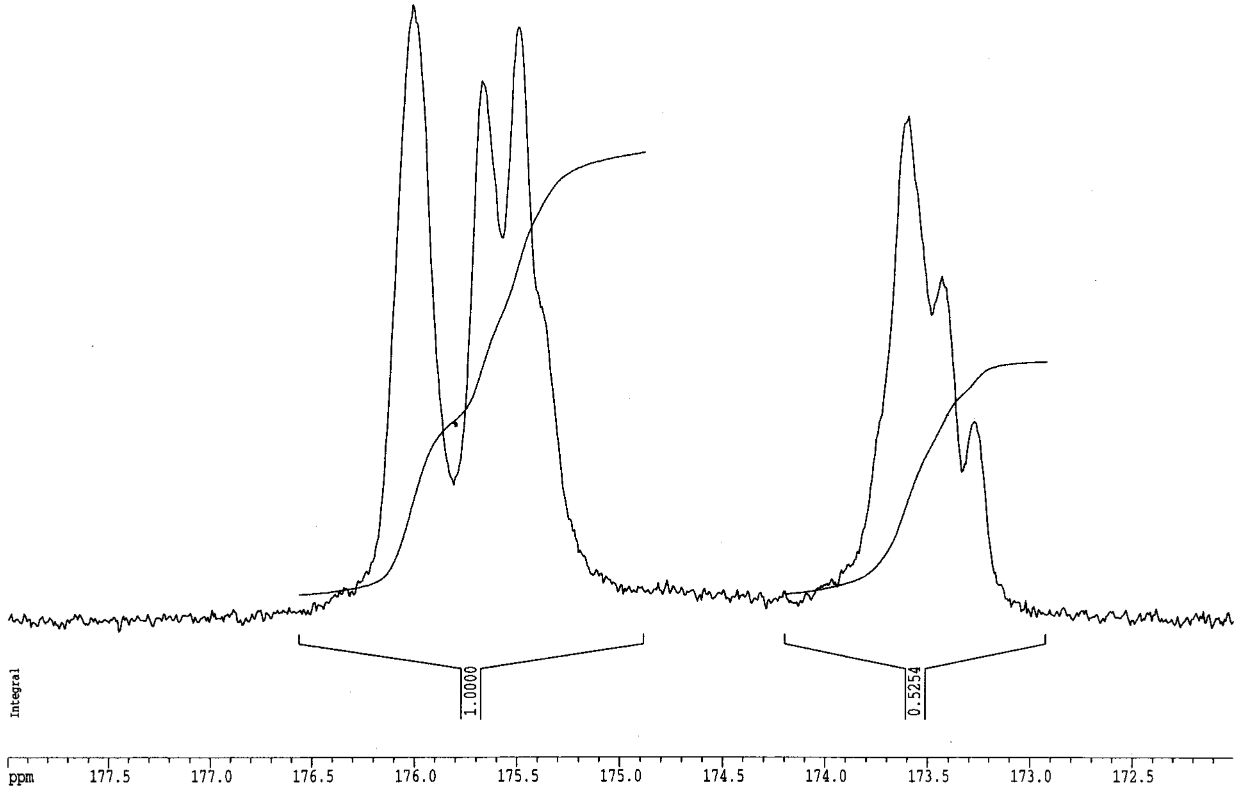

Figure 4. ^{13}C NMR spectrum of the PMA carboxyl carbon in 0.1 N HCl at 60 °C and 150 MHZ.

dent propagation steps the heptad probabilities are calculated with the help of P_r and P_m obtained from integrating the two carboxyl carbon groups as shown in Figure 4. The uncertainty in P_r given in Table 2 was estimated by varying the baseline and the integration intervals.

Lorentzian type peaks are fitted to the ^{13}C NMR spectrum of the carboxyl carbon atom resonances. The shifts of the resonances and their relative peak areas (peak area/total area of all peaks) are also given in Table 2. No deviations in the relative fitted peak area have been given because an increase in one area will mean a decrease in the other. The agreement between the relative fitted peak areas and the values of the calculated heptad probabilities in view of the limited resolution of the ^{13}C NMR spectra is rather satisfactory.

Under the assumption that chain growth proceeds by independent steps, the probability of racemic propagation is found to be 0.655. Then it follows that the numbers of monomers connected by consecutive r bonds

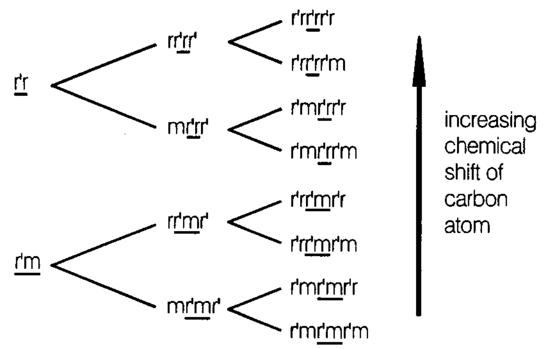

Figure 5. Illustration of the influences of near, next near, and next next near racemic and mesomeric bonds on the chemical shift of a PMA carboxyl carbon.

Table 2. Calculated Probabilities of Possible Racemic and Mesomeric Bond Sequences in PMA and the Chemical Shift Ranges and Shifts of Respectively the Backbone and Carboxyl Carbon

sequence	probability	carboxyl C	chemical shift, ppm	rel fitted peak area
triads				
$\underline{\text{r}'\text{r}}$	P_r	0.655 ± 0.015	175.2−176.2	0.639
$\underline{\text{r}'\text{m}}$	P_m	0.345 ± 0.015	173.1−173.9	0.361
heptads				
$\text{r}'\text{r}\ \underline{\text{r}'\text{r}}\ \text{r}'\text{r}$	$P_\text{r}P_\text{r}P_\text{r}$	0.281 ± 0.017	176.0	0.263
$\text{r}'\text{r}\ \underline{\text{r}'\text{r}}\ \text{r}'\text{m}$	$P_\text{r}P_\text{r}P_\text{m}$	0.148 ± 0.001	175.7	0.134
$\text{r}'\text{m}\ \underline{\text{r}'\text{r}}\ \text{r}'\text{r}$	$P_\text{m}P_\text{r}P_\text{r}$	0.148 ± 0.001	175.5	0.185
$\text{r}'\text{m}\ \underline{\text{r}'\text{r}}\ \text{r}'\text{m}$	$P_\text{m}P_\text{r}P_\text{m}$	0.078 ± 0.005	175.4	0.057
$\text{r}'\text{r}\ \underline{\text{r}'\text{m}}\ \text{r}'\text{r}$	$P_\text{r}P_\text{m}P_\text{r}$	0.148 ± 0.001	173.6	0.259
$\text{r}'\text{r}\ \underline{\text{r}'\text{m}}\ \text{r}'\text{m}$	$P_\text{r}P_\text{m}P_\text{m}$	0.078 ± 0.005	173.5	
$\text{r}'\text{m}\ \underline{\text{r}'\text{m}}\ \text{r}'\text{r}$	$P_\text{m}P_\text{m}P_\text{r}$	0.078 ± 0.005	173.4	0.074
$\text{r}'\text{m}\ \underline{\text{r}'\text{m}}\ \text{r}'\text{m}$	$P_\text{m}P_\text{m}P_\text{m}$	0.041 ± 0.005	173.3	0.029

have a distribution $p(n) = 0.655^{n-1} \times 0.345$. On hydrolysis each monomer yields two carboxylic acid groups connected by an r bond. From this fact it is found that about 72% of the acid groups on a given chain occur in r-bound stretches of six or more. As these stretches are isotactic the groups are close together, which enhances stabilization of carboxylate groups by hydrogen bonding.

Conclusions

Stereochemical configurations of PMA in 0.1 N HCl can be resolved with 150-MHz ^{13}C NMR at 60 °C.

Every other bond in PMA originates from a monomer and is therefore racemic. The other bond may either be racemic or mesomeric depending on the propogation step. The probability of racemic propagation is found to be 0.655 ± 0.015.

The longest stretch of carboxylic acids resolvable by ^{13}C NMR is six bonds long. The stretch of six racemic bonds has the largest probability.

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MA970495L