JOURNAL OF POLYMER SCIENCE: PART A-2 VOL. 6, 509-516 (1968)

# Identification of a Stereoblock Poly(methyl Methacrylate) Sample with a Stereocomplex

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## Synopsis

Acid hydrolysis of a stereoblock poly(methyl methacrylate) sample leads to a mixture of isotactic and syndiotactic poly(methacrylic acid) which can be separated by electrophoresis. The experiment confirms the stereochemical identity between the so-called "stereoblock" poly(methyl methacrylate) and the stereocomplex which syndiotactic and isotactic poly(methyl methacrylate) form in the ratio 2:1. A possible mechanism of replica polymerization is suggested to account for this effect.

Fox et al.[1] first reported the stereoregular polymerization of methyl methacrylate by using metalloorganic catalysts and photochemical initiation. These authors concluded that three different crystallizable types of poly(methyl methacrylate) (PMMA) could be obtained. In addition to the expected isotactic and syndiotactic polymers, which were later clearly identified,[2] these authors proposed the existence of a crystallizable stereoblock polymer characterized by high concentrations of both long isotactic and long syndiotactic sequences in the same chain. The condition for obtaining isotactic, syndiotactic, and stereoblock fractions of high steric purity are now very well defined,[3-7] and several physical criteria, based mainly on infrared and nuclear magnetic resonance spectra, have been developed to characterize them.[4,5,8-13]

A possible mechanism of stereoblock formation has been proposed by Coleman and Fox.[14] They discuss a two-state anionic polymerization of MMA which accounts easily and naturally[7,15] for the production of stereoblock polymers, especially in mixed solvents with highly complexing cations such as lithium. It has also, on the other hand, been observed that isotactic and syndiotactic PMMA mixtures crystallize to give a polymer with infrared, NMR, and x-ray diffraction spectra similar to those obtained in the case of stereoblock PMMA.[1,16-18] Recently Liquori and co-workers[19] published some detailed studies on a stereocomplex formed by the inter-

action of syndiotactic and isotactic PMMA[16,18,20] in polar solvents. In the solid state the stereocomplex is characterized by an interlocking of syndiotactic chains in open channels formed by the helical groove of isotactic chains. The ratio between syndiotactic and isotactic PMMA monomer units in the stereocomplex is 2:1. The same type of local interactions between monomer units persists in dilute solutions where the macromolecules are coiled.[21]

On the basis of these results and of the similarity of physical properties between the stereocomplex and the so-called stereoblock, Liquori et al.[19–21] suggested that stereoblock PMMA formed during the polymerization of methyl methacrylate under conditions reported by various authors[1,7,15,22–24] could be a complex between isotactic PMMA and syndiotactic PMMA.

Previous attempts to resolve the so-called stereoblock polymer into two components by chromatography[7] and fractional alkaline hydrolysis[25] apparently failed. By both methods 1:1 mixtures of isotactic and syndiotactic PMMA can be separated. In neither case, however, has an unambiguous proof of a "stereocomplex" fractionation been given. Glusker et al.[7] reported chromatographic separation of the two polymers but, according to their data the amount of eluted isotactic PMMA seems to amount to much less than half of the total eluted polymer, so the possibility is not ruled out that their data may show a separation between a syndiotactic-rich stereocomplex and the excess isotactic PMMA. Glavis's[25] hydrolysis experiment was performed starting from a chloroform solution of an isotactic–syndiotactic mixture, but chloroform does not seem to be a solvent which favors the complex formation. A point in favor of possible identity between stereoblock and stereocomplex PMMA's is the high crystallinity of both, since it is known that irregularly repeating sequences are difficult to crystallize. The possibility of separating certain stereoblock polymers of MMA into fractions differing in molecular weight and tacticity has, indeed, already been established;[7,22,23] it is the aim of this paper to illustrate a set of experiments which add some strong evidence in favor of a possible stereochemical identity between stereoblock PMMA and syndiotactic–isotactic (2:1) complexes.

It has been shown very recently[26] that isotactic and syndiotactic poly(methacrylic acids) migrate with different electrophoretic mobilities in an electric field. At a pH of about 5 the two polyelectrolytes can be separated by electrophoresis. No appreciable molecular weight dependence was found. We have, therefore, hydrolyzed the stereoblock PMMA, obtaining a poly(methacrylic acid) solution in which two electrophoretically different species, with mobility values very close to those of isotactic and syndiotactic poly(methacrylic acids) (PMA) already reported,[26] can be observed and separated at pH $\approx$ 5.

## Experimental

The stereoblock PMMA was synthesized by polymerizing MMA with 9-fluorenylithium[7] at −60°C. The toluene–THF (95:5) solvent was pre-

pared as follows. Toluene containing 0.5 g. of fluorene and 10 ml. of THF with 1.5 ml. of BuLi in a reaction flask were gently boiled for 1 hr.; toluene was added to obtain a 5% THF–95% toluene mixture. The reaction flask was put in a Dewar flask at −60°C., and 20 ml. of MMA was added. The polymerization was stopped after 1 hr. by adding methyl alcohol. The PMMA was purified by dissolving it in methylene chloride and precipitating with methanol. The precipitate was thoroughly washed with acetone, to eliminate soluble fractions, and vacuum dried.

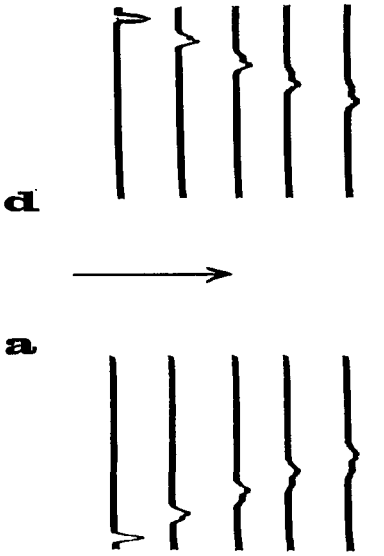


Fig. 1. Electrophoretic patterns of descending (d) and ascending (a) boundaries for run No. 3.

The NMR spectrum of the polymer in chloroform was recorded (see below, Fig. 3*A*) with a Varian A-60 A spectrometer.

The hydrolysis of the PMMA was carried out with concentrated sulfuric acid as proposed by Loebl and O'Neill.[27,28] Under these conditions the degradation of the polymer chain is very slight, as detected by determination of viscosity.[29–31] The degree of hydrolysis was 90–94%. Analytical electrophoretic measurements were performed at 4°C. with a Tiselius-Klett apparatus using the Philpot technique.[26,32]

Buffer solutions were made with $Na_2HPO_4$ at constant $Na^+$ concentration 0.03 eq./l.) and the pH was adjusted by addition of citric acid. Osmotic equilibrium was established between PMA and buffer solutions before every electrophoresis run by dializing each sample against the buffer for about one week with regular changes of the outer buffer solution.

The electrophoretic data on PMA obtained by hydrolysis of stereoblock PMMA are shown in Table I. Figure 1 shows the electrophoretic patterns of ascending and descending boundaries for run No. 3 at pH = 5.18.

Preparative electrophoretic separation has been achieved at $\sim 4°C.$ by the density gradient technique[32] in a 50 cm. column (5 cm. in diameter) at constant buffer concentration (0.03 eq./l. of $Na^+$ + citric acid at pH $\approx$ 5), with sucrose concentration ranging from 50 to 0%. From 12 to 15 ml. of 0.01*M* PMA (in buffer + 2–5% sucrose) was added at the right level in the column and gently stirred to build up a stable density gradient within the sample.[33]

The electrophoresis runs were made at constant current (40–70 ma.) until a clear separation was reached between the faster and the slower component. The power supply was an Alkos apparatus. The PMA motion could be easily followed by using a Wood lamp owing to a slight fluorescence of the sample originating, most probably, during the acid hydrolysis (the faster moving component was bluish and the slower moving one greenish).

TABLE I
Electrophoretic Separation of Isotactic and Syndiotactic Poly(methacrylic Acid) Obtained by Acid Hydrolysis of Stereoblock PMMA[a]

| Sample | pH | Specific conductivity $K \times 10^3$, cm.$^{-1}$ ohm$^{-1}$ | Current $i \times 10^3$, amp. | | Mobility, cm.$^2$/sec. · v.[b] $U_A \times 10^4$ | $U_D \times 10^4$ | $U_M \times 10^4$ |
|---|---|---|---|---|---|---|---|
| 1 | 4.94 | 1.33 | 1.063 | Faster | 1.42 | 1.40 | 1.41 |
| | | | | Slower | 1.21 | 1.20 | 1.205 |
| 2 | 5.19 | 1.26 | 0.922 | Faster | 1.43 | 1.44 | 1.435 |
| | | | | Slower | 1.26 | 1.26 | 1.26 |
| 3 | 5.18 | 1.27 | 1.023 | Faster | 1.50 | 1.44 | 1.47 |
| | | | | Slower | 1.34 | 1.30 | 1.32 |
| 4 | 7.50 | 1.60 | 1.019 | Single boundary | 2.19 | 2.02 | 2.10 |

[a] Buffer: $Na_2HPO_4$ + Citric acid at constant $Na^+$ concentration, 0.03 eq./l.; total PMA concentration: runs No. 1, 2, and 4, 0.0075 eq./l., run No. 3, 0.015 eq./l.

[b] $U_A$ = mobility of ascending boundary, $U_D$ = mobility of descending boundary, $U_M$ = Average mobility.

## Discussion

Experimental results reported in Table I and Figure 1 show that PMA obtained by acid hydrolysis of our stereoblock PMMA sample is a mixture of two different electrophoretic species which can be separated at pH $\approx$ 5. The mobilities of faster and slower moving species (Table I, last column) are very close to those found for isotactic and conventional (mainly syndiotactic) PMA (See ref. 25, Table I): i.e., $U_{iso} = 1.23 \times 10^{-4}$ and $U_{syndio} = 1.48 \times 10^{-4}$ cm.$^2$/sec.-v. In Figure 1, it can be seen that the amount of faster-moving PMA is approximately twice the amount of the slower-moving PMA.

At pH $\sim$ 7 no electrophoretic separation occurs, as must be expected for a mixture of isotactic and syndiotactic PMA;[26] this fact confirms that dif-

ferent mobilities do not arise from a possible difference in degree of hydrolysis of the two species.

In order to analyze further the relative amounts of the two components a density gradient, electrophoretic separation has been performed in a column of 1 cm. diameter with 0.2 ml. of PMA solution. After 15–20 cm. migration of the PMA, two clearly separated bands could be seen. The content of the column was then collected, drop by drop, in a $10^{-5}M$ acridine orange (AO) solution buffered at pH $\approx$ 7 with $0.001M$ sodium cacodylate. No more than 9–12 drops were collected in every 50 ml. of AO solution in order to have a high value for the ratio [AO]/[PMA]. The visible spectrum of the dye solution was recorded with a Beckman DK-2 spectrophotometer

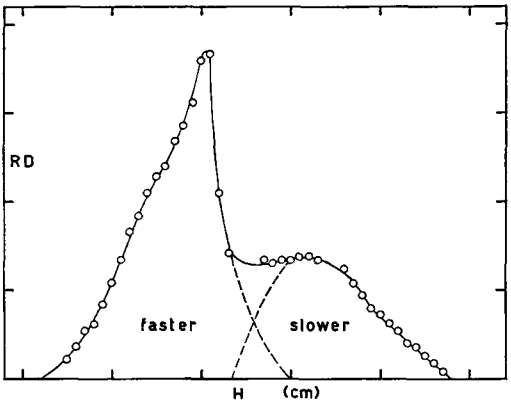


Fig. 2. Spectrophotometric analysis of density gradient electrophoresis of PMA at pH $\sim$ 5. *RD* denotes the relative decrease of acridine orange optical density ($\lambda$ = 492 m$\mu$), *H* is the height along the column. The ratio of faster to slower areas is $\sim$2.

after the addition of each drop. The relative decrease of the optical density of AO at 492 m$\mu$ is known to be proportional to the amount of polyelectrolyte in each drop.[34–36]

Figure 2 clearly shows the ratio 2:1 between faster- and slower-moving components. It is interesting to notice that the relative amounts of the two species is in agreement with the ratio 2:1 expected for a stereocomplex.[19,21]

Some amounts of faster- and slower-moving components have been also separated in density gradient columns as explained in the experimental section. The samples were dialyzed against distilled water, concentrated, and lyophylized. Viscosimetric molecular weights[29] of the two samples have been measured: $M_v$ (faster) $\simeq$ 110,000, $M_v$ (slower) $\simeq$ 70,000. The dried PMA samples were methylated in benzene solution with diazomethane. After methylation, the PMA was precipitated from the concentrated benzene solutions with *n*-hexane and vacuum dried.

On a 10% chloroform solution of each PMMA sample, NMR spectra were obtained; the results are shown in Figures 3*B* and 3*C*, and in Table II.

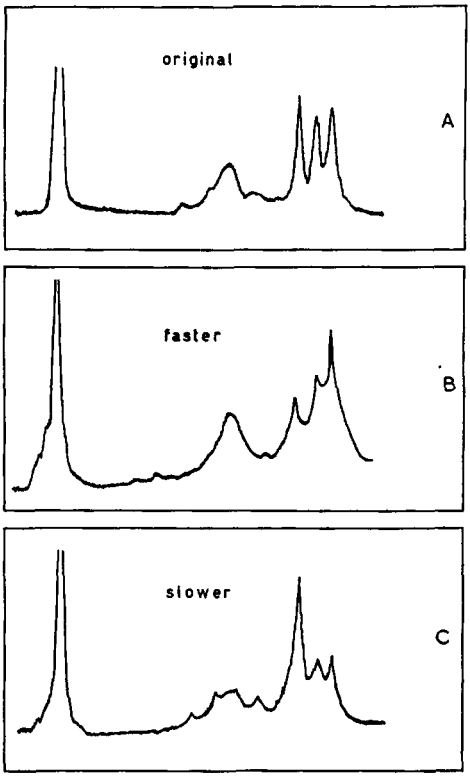


Fig. 3. Nuclear magnetic resonance spectra at PMMA in 10% chloroform solutions: (*A*) stereoblock PMMA; (*B*) PMMA from methylation of the faster-moving component; (*C*) PMMA from methylation of the slower-moving component.

The result of the experiments show that the so-called stereoblock PMMA synthesized in our Laboratory is a mixture of two components in the ratio 2:1; the first component is predominantly syndiotactic and the second isotactic. These results clearly confirm the suggestion of Liquori et al.[19] that stereoblock PMMA is a stereocomplex formed during the MMA polymerization. It must, however, be noted that these are the results of experiments carried out on a single sample PMMA, and additional preparations should be examined before generalizing the above conclusion.

TABLE II
Relative Areas for the $\alpha$-Methyl Peaks in the NMR Spectra of the Original Stereoblock PMMA and of the Sample Obtained after Methylation

| | 8.78 $\tau$ = ppm (isotactic) | 8.95 $\tau$ = ppm (heterotactic) | 9.09 $\tau$ = ppm (syndiotactic) |
|---|---|---|---|
| Original | 0.33 | 0.33 | 0.33 |
| Faster | 0.24 | 0.25 | 0.51 |
| Slower | 0.55 | 0.26 | 0.19 |

As to the degree of steric purity of the isotactic and syndiotactic components in the stereocomplex studied, it does not seem possible to decide clearly whether the impurity of the separated samples as judged from the NMR spectra can only be attributed to an imperfect separation. Although more experiments will be needed in order to clarify the above points further, a very interesting implication of the formation of a stereocomplex under conditions generally leading to polymers previously described as stereoblock emerges; i.e., the possibility that an ordered polymerization process takes place corresponding to a replica polymerization. This was already suggested long ago on purely speculative grounds.[37]

The authors are indebted to Dr. P. A. Temussi for running the NM spectra. This work has been carried out with the financial support of the Italian C.N.R.

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Received January 11, 1967
Revised July 25, 1967