

## A Novel Synthesis of Methyl Acrylate- $\alpha$ - $d$ and $^1\text{H}$ Nuclear Magnetic Resonance Spectra of Its Alternating Copolymers

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**ABSTRACT:** Methyl acrylate- $\alpha$ - $d$  of high isotopic purity was synthesized in 50 per cent yield by reducing methyl  $\alpha$ -bromoacrylate with zinc dust and deuterium oxide in diethylene glycol dimethyl ether at 80—100°C.  $^1\text{H}$  nuclear magnetic resonance spectra of alternating styrene- $\alpha$ - $d$ -methyl acrylate- $\alpha$ - $d$  and  $\alpha$ -methylstyrene-methyl acrylate- $\alpha$ - $d$  copolymers are discussed.

**KEY WORDS** Methyl Acrylate- $\alpha$ - $d$  / Deuteration / Zinc / Deuterium Oxide /  $^1\text{H}$  NMR / Alternating Copolymer /

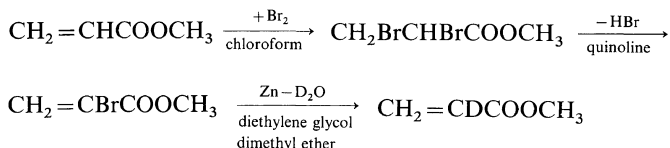
The partial deuteration of a vinyl monomer at a specified position has made possible the useful simplification of  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra of derived polymers.<sup>1</sup>

Matsuzaki *et al.*<sup>2</sup> synthesized methyl acrylate- $\alpha$ - $d$  by hydrolyzing acrylonitrile- $\alpha$ - $d$ <sup>3</sup> with  $\text{D}_2\text{O}$ - $\text{D}_2\text{SO}_4$  and esterifying the resulting acid with methanol. The yield however was low (14%) and the isotopic purity, unsatisfactory (91%).

The present paper describes a novel and simple synthesis of methyl acrylate- $\alpha$ - $d$  of high isotopic purity *via* readily available intermediates. The reaction scheme is

The last step, in which a deuterium is substituted for bromine, is an application of Whitesides *et al.*'s deuteration procedure.<sup>4</sup> They carried out the reaction on some saturated halogeno-esters and -nitriles.

Methyl acrylate- $\alpha$ - $d$  thus obtained was copolymerized to give alternating styrene- $\alpha$ - $d$ -methyl acrylate- $\alpha$ - $d$  and  $\alpha$ -methylstyrene-methyl acrylate- $\alpha$ - $d$  copolymers. The  $^1\text{H}$  NMR spectra of these copolymers are shown and the backbone  $\text{CH}_2$  spectra of the former copolymer determined at 60, 90, and 220 MHz are discussed by comparing them with computer-simulated spectra.



### EXPERIMENTAL

#### *Preparation of Methyl $\alpha$ -Bromoacrylate*

According to the literature,<sup>5</sup> bromine was added to methyl acrylate in chloroform below 5°C to give a 98% yield of methyl  $\alpha,\beta$ -dibromopropionate which was dehydrobrominated with an equimolar amount of quinoline at 60—80°C to methyl  $\alpha$ -bromoacrylate in an 86% yield.

#### *Zinc-Deuterium Oxide Reduction of Methyl $\alpha$ -Bromoacrylate*

In a three-necked flask equipped with a thermometer and a Vigreux column, zinc dust (30 g, 0.46 mol) was activated<sup>6</sup> by magnetic stirring with 2% hydrochloric acid (100 ml) for 1—2 min and washed successively with distilled water, ethanol, and diethyl ether. The zinc dust was suspended in diethylene glycol dimethyl ether (50 ml). To this

suspension, deuterium oxide (3 ml) and benzene (50 ml) were added and their azeotropic mixture was distilled to remove any possible source of protons from the flask and the surface of the zinc. Following the distillation, a small volume of diethylene glycol dimethyl ether was distilled under reduced pressure to expel the last trace of benzene which would otherwise contaminate the methyl acrylate- $\alpha$ - $d$ , since both compounds boil at 80°C. The zinc dust was subjected to a second activation by warming with ethylene dibromide (2 ml).

Then, to the flask, methyl  $\alpha$ -bromoacrylate (25 ml, 0.24 mol) and deuterium oxide (15 ml, 0.83 mol) were added and heated at 80–100°C with vigorous stirring. An exothermic reaction took place immediately and methyl acrylate- $\alpha$ - $d$  distilled out from the Vigreux column. When boiling became weak, volatile fractions were collected in a dry ice trap under moderately reduced pressure. The aqueous layer was saturated with sodium chloride and separated from the organic layer. The combined organic layers, containing methyl acrylate- $\alpha$ - $d$ , unchanged methyl  $\alpha$ -bromoacrylate, methanol, and diethylene glycol dimethyl ether, were dried over anhydrous sodium sulfate and fractionally distilled. Any methanol remaining was removed by redistilling the methyl acrylate- $\alpha$ - $d$  fraction after first adding phenyl isocyanate. The yield of pure product was 50%.

#### Alternating Copolymerization

Practically equimolar methyl acrylate- $\alpha$ - $d$  and styrene- $\alpha$ - $d$  or  $\alpha$ -methylstyrene were alternately copolymerized in the presence of 10 mol% (to acrylate) ethylaluminum sesquichloride in toluene at 0°C. The details of the copolymerization and work-up are described in our previous paper.<sup>7</sup>

#### Styrene- $\alpha$ - $d$

Styrene- $\alpha$ - $d$  was synthesized according to the literature<sup>8</sup> from acetophenone and LiAlD<sub>4</sub>. The present deuteration method could also be applied to synthesize this deuteromonomer in 50% yield and was less expensive. However, the precursor,  $\alpha$ -bromostyrene inevitably contained a few per cent of *trans*- $\alpha$ -bromostyrene which was difficult to remove and hence gave less pure styrene- $\alpha$ - $d$ .

#### Deuterium Oxide

Deuterium oxide was of Merck, d 99.75%.

#### Other Reagents

Other reagents were of commercially available Guaranteed or Extra Pure Grade and purified as usual.

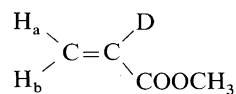
#### NMR Measurement

The <sup>1</sup>H NMR spectra of alternating copolymers were determined in deuteriochloroform at 60°C and in *o*-dichlorobenzene at 170°C. Sample concentrations were 5–10 w/v% and tetramethylsilane was used as an internal reference. A Hitachi R-20B spectrometer with a signal-averaging analyzer was used for 60 MHz measurement. A Hitachi R-40 spectrometer was used for the 90 MHz measurement and a Varian HR-220 spectrometer was used for the 220 MHz measurement.

## RESULTS AND DISCUSSION

#### Synthesis of Methyl Acrylate- $\alpha$ - $d$

Reduction of methyl  $\alpha$ -bromoacrylate by zinc dust and deuterium oxide gave methyl acrylate- $\alpha$ - $d$  in fairly good yield. It seemed important to use fresh and well-activated zinc dust to achieve a good product yield. The NMR spectrum of pure methyl acrylate- $\alpha$ - $d$  showed no absorptions for undeuterated acrylate. Therefore, the isotopic purity of the product is sufficiently high for the purpose of NMR simplification.



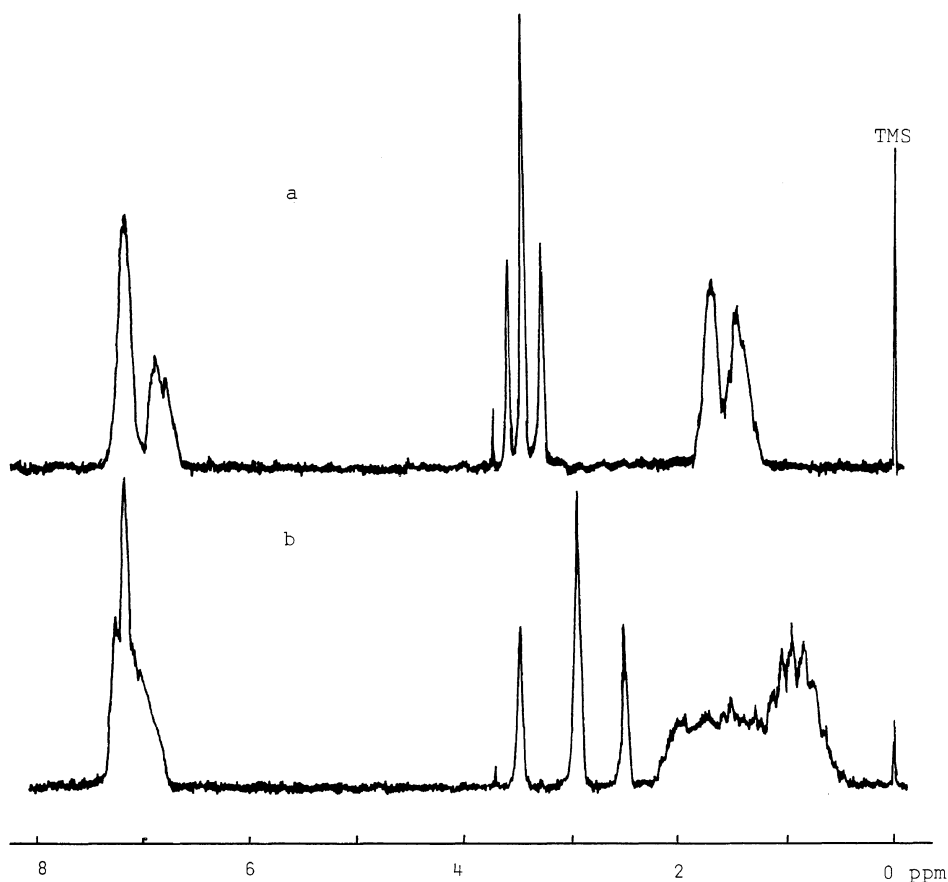
$\delta_{\text{OCH}_3}$  3.70,  $\delta_{\text{H}_a}$  5.75,  $\delta_{\text{H}_b}$  6.33 ppm,  $J_{\text{H}_a-\text{H}_b}$  1.70,  $J_{\text{H}_a-\text{D}}$  1.60,  $J_{\text{H}_b-\text{D}}$  2.61 Hz (10 w/v% in carbon tetrachloride)

The present method of synthesis of methyl acrylate- $\alpha$ - $d$  is superior to the method of ref 2, in terms of yield, isotopic purity, and availability of reagents.

#### <sup>1</sup>H NMR Spectra of Alternating Copolymers

Figure 1a and b show <sup>1</sup>H NMR spectra of alternating styrene- $\alpha$ - $d$ -methyl acrylate- $\alpha$ - $d$  and  $\alpha$ -methylstyrene-methyl acrylate- $\alpha$ - $d$  copolymers determined at 220 MHz in deuteriochloroform at 60°C.

The aliphatic region of alternating styrene- $\alpha$ - $d$ -



**Figure 1.** 220 MHz  $^1\text{H}$  NMR spectra of (a) the alternating styrene- $\alpha$ - $d$ -methyl acrylate- $\alpha$ - $d$  copolymer and (b) the alternating  $\alpha$ -methylstyrene-methyl acrylate- $\alpha$ - $d$  copolymer determined in deuteriochloroform at  $60^\circ\text{C}$ .

methyl acrylate- $\alpha$ - $d$  copolymer is very similar to the 300 MHz spectrum of the undeuterated copolymer reported by Harwood *et al.*<sup>9</sup> except that CH proton absorptions for styrene and methyl acrylate units have disappeared. The peak area ratio of aromatic to aliphatic proton absorption shows that this copolymer is of a 1 : 1 molar composition. The three sharp  $\text{CH}_3\text{O}$  peaks at 3.25, 3.45, and 3.58 ppm assigned to coisotactic (mm), coheterotactic (mr), and cosyndiotactic (rr) triads have the following intensity ratio.

$$\text{mm} : \text{mr} : \text{rr} = 28\% : 50\% : 22\%$$

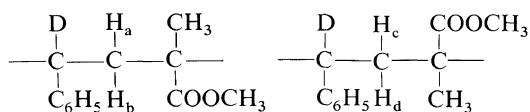
and give a coisotacticity value  $\sigma = 0.53$ , which is in good agreement with the value reported.<sup>7,9</sup> A negligibly small peak at 3.70 ppm (*ca.* 4%) is probably due to successive acrylate units. Poly-

(methyl acrylate- $\alpha$ - $d$ ) showed its  $\text{CH}_3\text{O}$  absorption at 3.65 ppm.

The upper half of Figure 2 shows the observed backbone  $\text{CH}_2$  spectra determined at 60, 90, as well as 220 MHz. Whereas the 220 MHz spectrum appears as two broad peaks of identical intensity, the 60 and 90 MHz spectra appear as asymmetric broad AB quartets.

The backbone  $\text{CH}_2$  spectrum of the alternating styrene- $\alpha$ - $d$ -methyl methacrylate copolymer, previously reported by us,<sup>7</sup> showed eight peaks of two AB quartets for coisotactic (m) and cosyndiotactic (r) dyads. The two dyads possessed appreciably different parameters to each other.

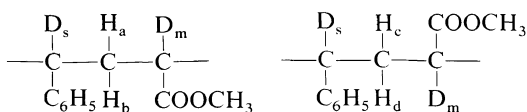
Synthesis of Methyl Acrylate- $\alpha$ - $d$



coisotactic dyad (m)      cosyndiotactic dyad (r)

$$\delta_{\text{H}_b} - \delta_{\text{H}_a} = 0.55 \text{ ppm} \quad \delta_{\text{H}_d} - \delta_{\text{H}_c} = 0.21 \text{ ppm}$$

The present copolymer, alternating styrene- $\alpha$ - $d$ -methyl acrylate- $\alpha$ - $d$ , shows, at a glance, only one (though broad) AB quartet instead of the expected two AB quartets. Substitution of deuterium for the methyl group (methacrylate to acrylate- $\alpha$ - $d$ ) brings the two CH<sub>2</sub> of coisotactic and cosyndiotactic dyads into a similar magnetic environment through the easier molecular motion of this copolymer.



coisotactic dyad (m)      cosyndiotactic dyad (r)

The lower half of Figure 2 shows computer-simulated spectra which should give the best result at the three radio frequencies. To explain the broad and asymmetric absorptions, it is assumed that the center

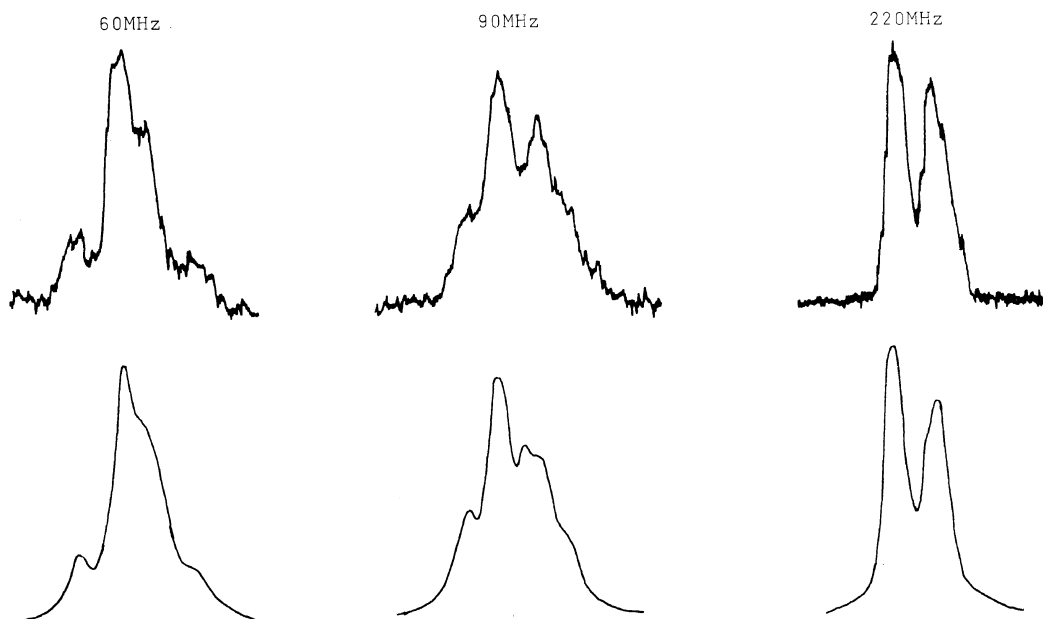
of the coisotactic dyad is placed in a 0.0414 ppm higher magnetic field than the center of the cosyndiotactic dyad. The most preferable parameters are

Coisotactic dyad	Cosyndiotactic dyad
$\delta_{\text{H}_b} - \delta_{\text{H}_a} = 0.3218 \text{ ppm}$	$\delta_{\text{H}_d} - \delta_{\text{H}_c} = 0.2273 \text{ ppm}$
$J_{\text{H}_a - \text{H}_b} = -13.2 \text{ Hz}$	$J_{\text{H}_c - \text{H}_d} = -13.2 \text{ Hz}$
$J_{\text{H}_a - \text{D}_s} = 1.5 \text{ Hz}$	$J_{\text{H}_c - \text{D}_s} = 1.5 \text{ Hz}$
$J_{\text{H}_a - \text{D}_m} = 1.5 \text{ Hz}$	$J_{\text{H}_c - \text{D}_m} = 0.4 \text{ Hz}$
$J_{\text{H}_b - \text{D}_s} = 0.4 \text{ Hz}$	$J_{\text{H}_d - \text{D}_s} = 0.4 \text{ Hz}$
$J_{\text{H}_b - \text{D}_m} = 0.4 \text{ Hz}$	$J_{\text{H}_d - \text{D}_m} = 1.5 \text{ Hz}$

$$\text{Intensity ratio, } m : r = 0.53 : 0.47$$

The coisotactic dyad is centered at 0.0414 ppm higher magnetic field than the cosyndiotactic dyad. Peak width: 3.0, 4.5, and 11.0 Hz for 60, 90, and 220 MHz, respectively.

The agreement between the observed and the simulated spectra is good but not as good as we found for the alternating styrene- $\alpha$ - $d$ -methyl methacrylate copolymer. For the present simulation, we had to input peak widths which are proportional



**Figure 2.** Backbone CH<sub>2</sub> spectra of the alternating styrene- $\alpha$ - $d$ -methyl acrylate- $\alpha$ - $d$  copolymer at various radio-frequencies: (above) observed, and (below) simulated spectra.

to the ratio-frequencies. This may suggest that further remote sequences or the conformation of the copolymer should be partly taken into consideration for a more complete simulation.

Figure 1b shows a 220 MHz spectrum of the alternating  $\alpha$ -methylstyrene-methyl acrylate- $\alpha$ -d copolymer. The CH<sub>3</sub> and CH<sub>2</sub> absorptions are so complicated that they provide no useful information on the configuration.

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