Registry No. Benzoyl peroxide, 94-36-0; polystyrene, 9003-53-6.

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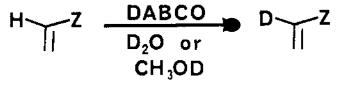
Facile Synthesis of α-Deuteriated Acrylates and Activated Vinyls

Enormous capability exists for studying reaction mechanisms and the solution and solid-state behavior of small molecules and polymers by ^{2}H NMR. In polymer characterization, for example, the molecular relaxation times available by using variable-temperature wide-line techniques spans the range of characteristic frequencies from ca. 10 MHz to 1 Hz.[1] In addition, deuteriated polymers can also be studied by neutron scattering, isotope-shifted bands in the infrared, and pyrolysis–GC–MS. New methods of deuterium incorporation at pivotal positions are vital for expanded use of these techniques.

An additional advantage in using deuteriated reactants in synthesis is that ^{2}H NMR can be used directly to follow conversion, monitor intermediate formation and disappearance, and examine side reactions and by-products. The present discovery stems from the combined use of ^{1}H, ^{2}H, and ^{13}C solution spectroscopy to monitor the synthesis of a deuteriated monomer needed for another study.[2] The specific reaction under investigation involved functionalization of acrylate esters by reaction with aldehydes in the presence of DABCO.[3] In the absence of acceptor aldehydes, and in the presence of a suitable exchangeable deuterium donor, rapid incorporation of deuterium at the α position was observed for a number of activated vinyl species (1 → 2). Table I summarizes our initial results.



1 2

Z = CO_2R, CN, COR

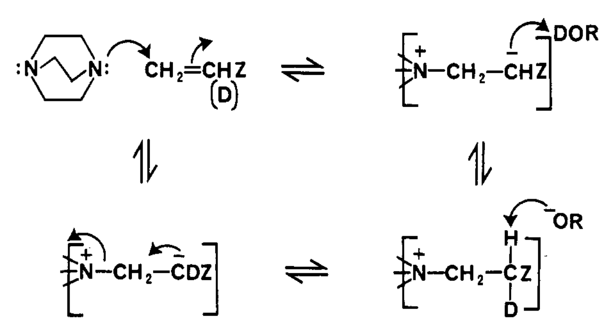


Figure 1. Proposed mechanism for α-H/D equilibration.

Table I
Summary of Reaction Conditions

compound	reactn conditions	% deuterium[a] found	% deuterium[a] theor
methyl acrylate	30 min/CH_3OD	93.7	91.6
butyl acrylate	30 min/CH_3OD	81.8	93.7
acrylonitrile	30 min/CH_3OD	90.5	88.2
acrylonitrile	10 min/D_2O	82.0	94.0
acrylonitrile	after second exchange	92.7	96.0

[a] Determined by integration of the vinyl region of the ^{1}H NMR spectra.

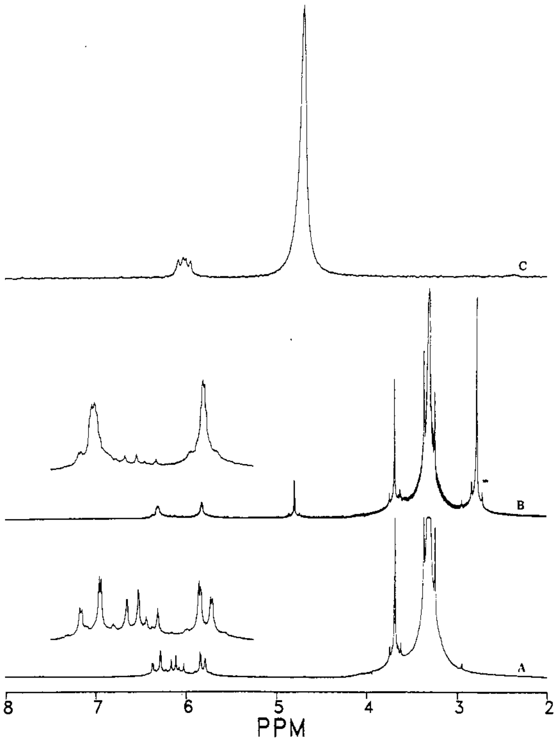


Figure 2. (A) ^{1}H spectrum of undeuteriated methyl acrylate, (B) ^{1}H spectrum of methyl acrylate-α-*d*, and (C) ^{1}H-coupled ^{2}H spectrum of methyl acrylate-α-*d*.

We propose a DABCO-catalyzed equilibration (Figure 1) in which deuterium incorporation can be driven to high levels by use of a large excess of the deuterium donor. Levels of incorporation greater than 80% were obtained in minutes with a single exchange process. This procedure is straightforward in contrast to previously reported multistep methods of α-deuteriation of acrylates.[4-6]

While either CH_3OD or D_2O served in the exchange for acrylonitrile, hydrolysis of the intermediate species formed from acrylate esters occurred in D_2O. In addition, higher alkyl esters underwent minor transesterification to methyl acrylate if the exchange reaction was extended. Exchange of methyl vinyl ketone was complete in a matter of min-

Table II
Summary of Coupling Constants

	^{1}H NMR			^{2}H NMR		^{13}C NMR
compound	$^3J_{AB}$	$^3J_{AX}$	$^3J_{BX}$	$^3J_{D\text{-}A}$	$^3J_{D\text{-}B}$	$^1J_{C\text{-}D}$
methyl acrylate[a]	1.51	17.3	10.2	2.61	1.57	25.9
butyl acrylate	1.68	17.3	10.3	2.57	1.61	25.0
acrylonitrile (D_2O)				2.68	1.77	27.4
acrylonitrile		17.6	11.7	2.64	1.84	26.8

[a] Deuterium donor was MeOD except for D_2O for entry three.

utes, although prolonged reaction led to Michael addition and aldol condensation products.[7]

The general procedure involves simply mixing together excess deuterium donor with the activated substrate, adding DABCO, and monitoring the reaction with ^{1}H or ^{2}H NMR. The first trial was performed with a MeOD to methyl acrylate ratio of 13:1, with subsequent trials using a ratio to give a theoretical percent deuteration of greater than 95%. Figure 2 gives representative spectra for methyl acrylate. The vinylic region of the ^{1}H spectrum displays a typical ABX pattern with coupling constants $^3J_{AB} = 1.5$, $^3J_{AX} = 17.3$, and $^3J_{BX} = 10.2$ Hz. The A and B represent the *E* and *Z* hydrogens, respectively. The deuterium spectrum displays splitting of the α-^{2}H by the trans and cis hydrogens with $^3J_{D\text{-}A} = 2.52$ and $^3J_{D\text{-}B} = 1.57$ Hz, respectively. Essentially complete ^{1}H–^{2}H equilibration was observed in most cases, e.g., for methyl acrylate, 94% found versus 92% theoretical.

The deuterium exchange using acrylonitrile was performed twice by using D_2O to give a final percent deuteriation of 93.7%. This reaction was run interfacially, and upon separation and drying, the deuteriated acrylonitrile was isolated. NMR and FTIR were used to confirm deuteriation at the α position. Coupling constants for acrylonitrile were determined to be $^3J_{AX} = 17.6$ and $^3J_{BX} = 11.7$ Hz. The deuterium splitting of the α-^{2}H was $^3J_{D\text{-}A} = 2.68$ and $^3J_{D\text{-}B} = 1.77$ Hz. Table II summarizes coupling constants, in hertz, for the ^{1}H, ^{2}H, and ^{13}C spectra. For identical coupling paths the ratio of hydrogen–hydrogen coupling constants to hydrogen–deuterium constants range from 6.4 to 6.7.

These labeled materials, in addition to their value in forming specifically labeled polymers, should be useful in probing mechanisms in organic and natural product syntheses involving a variety of Grignard, Michael, and Diels–Alder reactions.

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Registry No. 1 (Z = Co_2Me), 96-33-3; 1 (Z = $CO_2(CH_2)_3Me$), 141-32-2; 1 (Z = CN), 107-13-1; 2 (Z = CO_2Me), 15020-05-0; 2 (Z = $CO_2(CH_2)_3Me$), 112741-03-4; 2 (Z = CN), 4635-82-9; DABCO, 280-57-9; MeOD, 4206-31-9; D_2O, 7789-20-0; methyl vinyl ketone, 78-94-4; methyl vinyl ketone (α-deuteriated), 112741-04-5.

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Chain Diffusion of Polystyrene in CS_2

Since Wellinghoff et al.[1] found that atactic polystyrene can form a thermally reversible gel in various solvents, several further investigations[2-5] have ensued to understand the nature of the physical gelation. Tan et al.[2] and Boyer et al.[3] proposed that chain overlap is responsible for the gelation, whereas Gan et al.[5] suggested the formation of microcrystal in the gel state to explain their observation of the enhanced low-angle light scattering in the gel state. From calorimetry measurement, the concentration of the physical cross-links in the gel structure was estimated to be 5–10% by François et al.[6] Despite these efforts, the chain configuration in the gel state is not fully understood, and it demands further examination. In this experiment, the forced Rayleigh scattering (FRS) technique was used to study the translational diffusion of the individual polymer chains in the gel state. Our previous experiment on gelatin[7] showed that self-diffusion is quenched below the gel point. Whether chain diffusion is also quenched in polystyrene/CS_2 gel is a burning question. This paper is focused on the issue of self-diffusion of polystyrene chains in CS_2 above and below the gelation region. By examining the self-diffusion we hope to shed some light on the nature of this gelation phenomenon.

Experimental Section. Polystyrene was obtained from Pressure Chemical Co. ($M_w/M_n = 1.06$ and 1.04 for 35K and 90K samples, respectively). Dye-labeled polystyrene was prepared by reacting randomly and sparsely *p*-aminomethylated polystyrene with *p*-azobenzoyl chloride as described elsewhere.[8] The labeling content was about 1 dye moiety/400 monomer units.

Polystyrene containing less than 30% of the labeled chain was dissolved in carbon disulfide (HPLC grade, Aldrich Chemical), filtered through a 0.4-μm filter twice, and then placed in a 5-mm path length cuvette. After the sample was initially stabilized at 25 °C for 24 h, the temperature was lowered at a rate of less than 0.5 °C/min to −24 °C and then raised to a desired temperature, at which FRS measurements were performed. The sample was stabilized at each temperature for at least 12 h prior to the measurements. Afterwards, the temperature was varied again in the same manner, and the gelation was checked visually (sample cell tilting, as performed by Tan et al.[2]). Both gel *formation* upon lowering the temperature $T_{gel,f}$ and gel *melting* upon raising the temperature, $T_{gel,m}$, were reproduced within 1 °C, and they are indicated by arrows in Figures 2 and 3. We found invariably $T_{gel,f} < T_{gel,m}$. We also note that the concentrations chosen for the experiment, 25 wt % of 35K and 18 wt % of 90K molecular weight, are in the semidilute solution region while they are not yet in the entanglement concentration region, $C^* < C < C_e$, where $C_e = \rho M_c/M$ with ρ being the polystyrene bulk density and $M_c = 35\,000$.

The experimental details of the FRS measurement have been described elsewhere.[9,10] The data analysis here re-

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