

SHORT COMMUNICATION

## The Formation of Butane in the Polymerization of Methyl Methacrylate with Butyllithium

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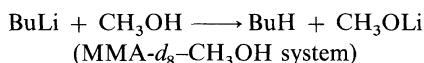
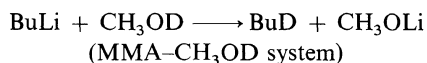
It has been found that a small amount of butane is formed when the polymerization of methyl methacrylate is initiated with butyllithium and terminated with acetic acid. The origin of the butane was not clear, although the proton abstraction from the monomer is assumed.<sup>1</sup>

In this work the polymerizations of undeuterated (MMA) and perdeuterated (MMA-*d*<sub>8</sub>) methyl methacrylates were initiated with undeuterated butyllithium (BuLi) and terminated by CH<sub>3</sub>OD and CH<sub>3</sub>OH, respectively. Deuterium distributions in the butane formed were determined by combined gas-liquid phase chromatography-mass spectrometry. Based on these results, the origin of the butane is discussed in this paper.

MMA-*d*<sub>8</sub> was prepared from acetone cyanohydrin-*d*<sub>7</sub> and methanol-*d*<sub>4</sub> according to the method of Crawford.<sup>2</sup> MMA or MMA-*d*<sub>8</sub> (10 mmol) was polymerized with BuLi (1 mmol) in either toluene or tetrahydrofuran (10 ml) at -78°C in a glass ampoule and terminated by adding a small amount of CH<sub>3</sub>OH or CH<sub>3</sub>OD. The volatile compounds were then distilled from the reaction mixture on the vacuum line. From the distillate, the low-boiling fraction was collected again by fractional distillation and subjected to analysis for the butane fraction by combined vapor-phase chromatography-mass spectrometry. The mass spectra were recorded by a JMS-01SG-2 mass spectrometer (JEOL) combined with a gas-liquid phase chromatograph.

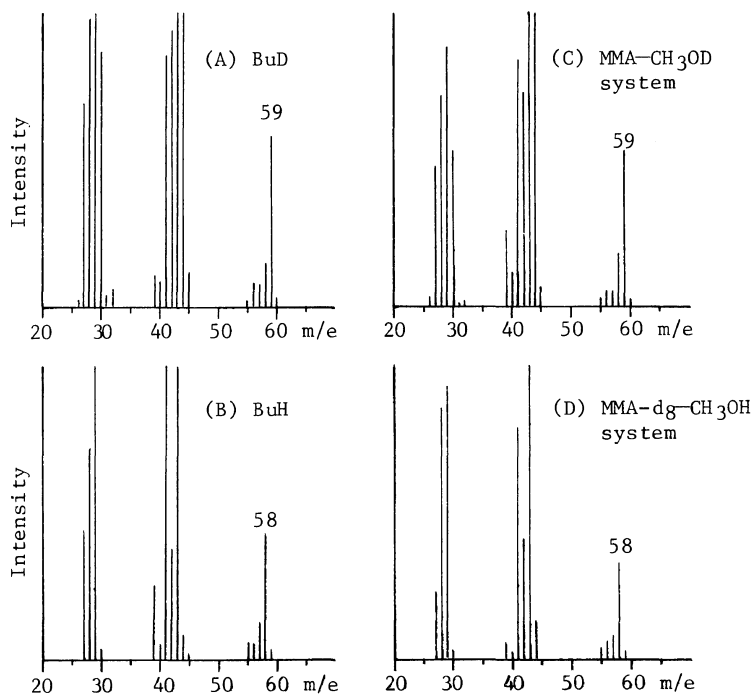
In Figure 1 are illustrated the mass spectra of the butanes formed in the products of the two poly-

merization reactions in toluene: (1) the polymerization of MMA terminated by CH<sub>3</sub>OD (MMA-CH<sub>3</sub>OD system) and (2) that of MMA-*d*<sub>8</sub> terminated by CH<sub>3</sub>OH (MMA-*d*<sub>8</sub>-CH<sub>3</sub>OH system). The reactions were quenched at 10 min following the initiation. The spectra of butane (BuH) and butane-*d*-1, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>D, (BuD) are also shown for comparison. The BuH and BuD were obtained by the reaction of BuLi with CH<sub>3</sub>OH and CH<sub>3</sub>OD, respectively. By inspecting these four spectra, it can be seen that the butane from the MMA-CH<sub>3</sub>OD system mainly consists of BuD and the butane from the MMA-*d*<sub>8</sub>-CH<sub>3</sub>OH system is mainly BuH. The results clearly indicate that a certain amount of BuLi remained unreacted even after 10 minutes following the initiation, and reacted with methanol to produce butane in the termination reaction.



Gas-chromatographic analysis showed that the butane formed corresponds to about 10% of the BuLi used.

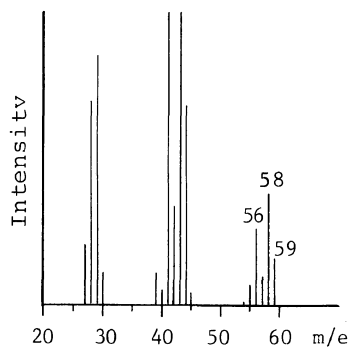
It has been reported that in the polymerization of MMA with fluorenyllithium in toluene at -78°C, the initiator disappeared instantaneously on mixing the reactants.<sup>3</sup> BuLi has a greater tendency to exist in an associated form in a nonpolar solvent in contrast to fluorenyllithium. Thus, the remaining



**Figure 1.** Mass spectra of butane-1-*d* (BuD) (A), butane (BuH) (B), the butane from MMA-CH<sub>3</sub>OD (C) and MMA-*d*<sub>8</sub>-CH<sub>3</sub>OH (D) systems in toluene for 10 min.

unreacted BuLi in the polymerization of MMA in toluene should be in a stable association form even in the presence of a small amount of this polar monomer. A similar phenomenon was observed by Vankerckhoven and Van Beylen in the polymerization of methacrylonitrile with BuLi in toluene at  $-78^{\circ}\text{C}$ , and the existence of the strongly associated and inactive form of BuLi was suggested.<sup>4</sup>

In the mass spectrum of the butane fraction for the MMA-CH<sub>3</sub>OD system after 12 h of reaction in toluene (Figure 2), the intensities of the peaks at  $m/e=58$  and 56 increase considerably compared with those in the spectrum of the butane from the polymerization for 10 min (Figure 1). The increasing peak intensity at  $m/e=58$  indicates that the hydrogen abstraction from the monomer or the polymer by the remaining BuLi occurs gradually during the polymerization reaction. On the other hand, enhancement in the peak intensity at  $m/e=56$  probably means that the prolonged polymerization time brings about the formation of butene from the remaining BuLi. The mechanism for this formation

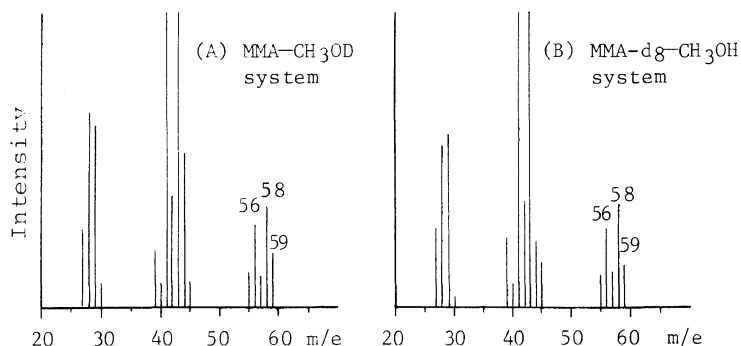


**Figure 2.** Mass spectrum of the butane fraction from MMA-CH<sub>3</sub>OD system in toluene for 12 h.

is not clear at the present.

Figure 3 shows the mass spectra of the butane from MMA-CH<sub>3</sub>OD and MMA-*d*<sub>8</sub>-CH<sub>3</sub>OH polymerization systems for 10 min. in tetrahydrofuran. The amount of butane measured by gas-liquid chromatography was about 5% of the BuLi used. Comparison of these spectra with those in Figure 1

Formation of Butane in the Polymerization of MMA with BuLi



**Figure 3.** Mass spectra of the butane fractions from MMA-CH<sub>3</sub>OD (A) and MMA-d<sub>8</sub>-CH<sub>3</sub>OH (B) systems in tetrahydrofuran for 10 min.

clearly indicates that the butane from the polymerizations in tetrahydrofuran contained an appreciable amount of the butane formed through the proton abstraction from the monomer or the polymer. The high polarity of the solvent may break down the association form of BuLi to reduce the amount of the remaining BuLi and enhance the abstraction reaction. The peak intensity at  $m/e=58$  in the spectrum of the butane from the MMA-CH<sub>3</sub>OD system was stronger than that of the peak at  $m/e=59$  in the spectrum of the butane from the MMA-d<sub>8</sub>-CH<sub>3</sub>OH system. This might indicate the isotope effect in the proton abstraction reaction by butyllithium in tetrahydrofuran. The formation of butene was also enhanced in tetrahydrofuran, as is evidenced by the increasing intensity of the peak at

$m/e=56$  in the spectra.

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