Polymer Bulletin 21, 489-495 (1989)

Polymer Bulletin

# On-line GPC/NMR analyses of block and random copolymers of methyl and butyl methacrylates prepared with $t$-$C_4H_9MgBr$

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## SUMMARY

The isotactic block and random copolymers of methyl methacrylate and butyl methacrylate prepared with $t$-$C_4H_9MgBr$ in toluene, were analyzed by using a 500 MHz $^1H$ NMR spectrometer as a detector of gel permeation chromatography. The molecular weight dependence of the chemical compositions of these copolymers could be directly determined with this method by monitoring signal intensities of $OCH_3$ and $OCH_2$ due to methyl methacrylate and butyl methacrylate units, respectively. From the results mechanism of the copolymerizations was discussed in some detail.

## INTRODUCTION

The properties of copolymers depend primarily on their chemical compositions, and the chemical compositions of copolymers often depend on their molecular weights. Molecular weight dependence of the compositions of copolymers has been determined by fractionation and subsequent compositional analysis of the fractions. However, this method requires much time and rather large amount of sample. A recent review (1) by Mori describes that dual-detector systems, such as UV-refractive index (RI), or multiple wave-lengths detections with an IR or UV detector, can be used for the determination of copolymer composition in gel permeation chromatography (GPC). In these methods, the monomer units to be distinctively detected are often limited by either their molecular structure or their combination.

Rapid progress has been made in NMR spectrometer on its sensitivity and resolution by introduction of superconducting magnet. Recent publications (2,3,4) demonstrated the feasibility of NMR spectrometer as a detector for high performance liquid chromatography. Recently we reported that the on-line GPC/NMR method using a 500 MHz $^1H$ NMR spectrometer was useful for analyzing the molecular weight and structure of polymers (5,6). In this work, the potential feasibility of the GPC/NMR method has been realized in the analysis of the chemical compositions of block and random copolymers of methyl methacrylate (MMA) and butyl methacrylate ($n$-BuMA) obtained by anionic polymerization. The molecular weight dependencies of the chemical compositions of these copolymers determined by the GPC/NMR experiment gave us important information on the copolymerization mechanism.

## EXPERIMENTAL

MMA and $n$-BuMA were purified by fractional distillation, dried over calcium dihydride, and then distilled under high vacuum just before use.

$t$-$C_4H_9MgBr$ was prepared from $t$-$C_4H_9Br$ and magnesium in dry diethyl ether ($[Mg]/[t\text{-}C_4H_9] = 1.28$).

Toluene, purified in a usual manner and stored over sodium metal, was mixed with a small amount of *n*-$C_4H_9Li$ and then vacuum-distilled.

The block copolymerization was carried out under dry nitrogen in a separable flask equipped with a mechanical stirrer. The polymerization of the first monomer, MMA, was initiated by adding the *t*-$C_4H_9MgBr$ solution to the monomer solution in toluene at -60°C. After 4.5 hr, toluene and then the second monomer, *n*-BuMA, were slowly added to the reaction mixture with stirring. The random copolymerization was carried out in a glass ampoule under dry nitrogen. The reaction was initiated by adding the *t*-$C_4H_9MgBr$ solution to a 2:1 mixture of MMA and *n*-BuMA in toluene at -78°C. Both copolymerizations were terminated by adding a small amount of methanol to the reaction mixture. The solvent and unreacted monomers were removed from the reaction mixture by vacuum distillation. The residues were dissolved in benzene, and the insoluble materials were removed by centrifugation, and the copolymers were recovered from the benzene solutions by freeze drying.

The on-line GPC/NMR system consisted of a JEOL JNM-GX500 spectrometer and a JASCO TRI ROTAR-V chromatograph equipped with a Shodex GPC column K-80M (30cmx0.8cm, maximum porosity=$3x10^7$). Further details of the system was described in the previous report (5). Chloroform-d was used as an eluent and the flow rate was 0.2 ml/min. The $^2D$ NMR signal of the eluent was satisfactorily intense for internal lock and shimming of the magnetic field. The background signals due to the small amount of impurities in the eluent, except for the signal of $H_2O$, were completely eliminated by subtracting the base line absorbance. Sixty degree pulse and the repetition time of 1.0 s were employed in the $^1H$ NMR measurement. The injected sample was 1.0 mg each. The $^1H$ NMR data, each consisted of 8192 data points covering 4500 Hz, were collected over the entire chromatographic peak and stored as 24 coadded scans every 24 s. A line broadening factor of 0.55 Hz was applied.

A Shodex SE-61 RI detector was also used for the detection.

## RESULTS AND DISCUSSION

Polymerization of MMA by *t*-$C_4H_9MgBr$ in toluene at low temperature gives highly isotactic PMMA with narrow molecular weight distribution (MWD) (7,8). The polymerization system is living and permits us to prepare the block copolymer of MMA with other methacrylates (9). In this work, the PMMA-*block*-poly(*n*-BuMA) was prepared by the polymerization of *n*-BuMA with the living isotactic PMMA formed with *t*-$C_4H_9MgBr$ in toluene at -60°C. The poly(MMA-*ran*-*n*-BuMA) was prepared by adding *t*-$C_4H_9MgBr$ to the mixture of MMA and *n*-BuMA ($[MMA]_0/[n\text{-BuMA}]_0=2/1$) in toluene at -78°C. The results of these copolymerizations are shown in Table 1. The number average molecular

Table 1 Preparation of Poly(MMA)-*block*-poly(*n*-BuMA) and Poly(MMA-*ran*-*n*-BuMA) with *t*-$C_4H_9MgBr$ in Toluene[a]

| | MMA/*n*-BuMA in feed | $[M]_0/[I]_0$ | Time (hr) | Yield (%) | Mn (VPO) | $\frac{Mw}{Mn}$ | MMA/*n*-BuMA in polymer[b] | Tacticity(%) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | mm | mr | rr |
| *Block*[c] | 34.4/65.6 | 87.5 | 4.5+24 | 100 | 10500 | 2.44 | 34.3/65.7 | 97 | 3 | 0 |
| *Random*[d] | 66.3/33.7 | 101.0 | 72 | 99 | 11200 | 3.88 | 67.2/32.8 | 97 | 3 | 0 |

[a] $[MMA+n\text{-BuMA}]_0$/toluene = 2.0 mol/L.

[b] Determined from $^1H$ NMR spectra measured in $CDCl_3$ at 35°C.

[c] MMA 40mmol, *n*-BuMA 76.4mmol, temperature -60°C; Mn(calcd)=11100.

[d] MMA 6.7mmol, *n*-BuMA 3.4mmol, temperature -78°C; Mn(calcd)=11500.

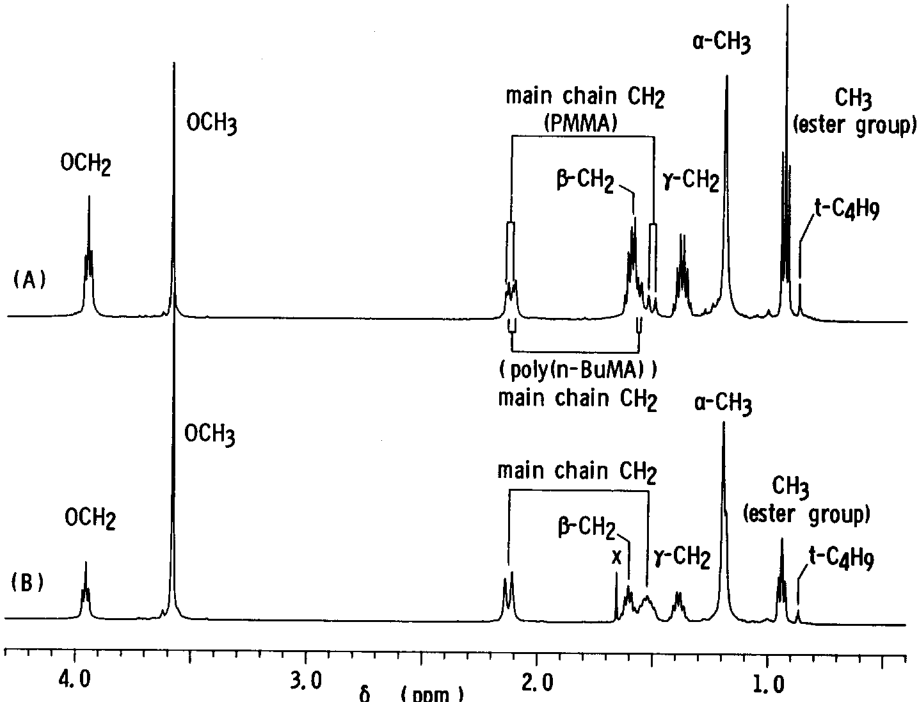

*Figure 1* 500 MHz $^1$H NMR spectra of PMMA-*block*-poly(*n*-BuMA) (A) and poly(MMA-*ran*-*n*-BuMA) (B) prepared with *t*-$C_4H_9MgBr$ in toluene at -60°C and -78°C, respectively ($CDCl_3$, 35°C)

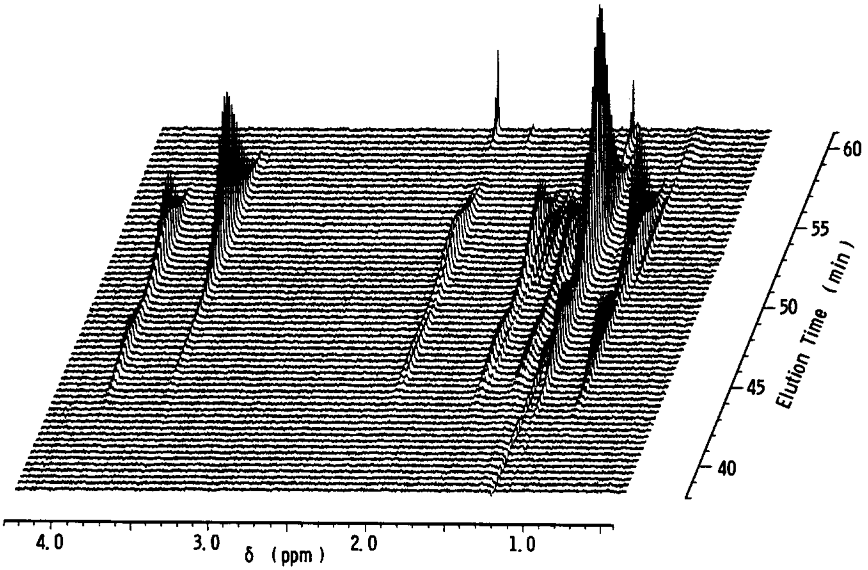

*Figure 2* On-line GPC/NMR data of PMMA-*block*-poly(*n*-BuMA) prepared with *t*-$C_4H_9MgBr$ in toluene at -60°C

weight (Mn) of the copolymers agreed well with the expected value, indicating the initiator efficiency to be close to unity, although multimodal MWD's were observed. Figure 1 shows 500 MHz $^1H$ NMR spectra of the copolymers measured in $CDCl_3$ at 35°C. It is evident from the $\alpha$-$CH_3$ and $CH_2$ signals that the copolymers are highly isotactic.

Figure 2 shows the GPC/NMR data of the PMMA-*block*-poly(*n*-BuMA). The GPC chromatograms corresponding to MMA and *n*-BuMA units can be obtained form the cross sections at 3.59ppm ($OCH_3$) and 3.95ppm ($OCH_2$), respectively. Relative intensities of the chromatograms were normalized to represent the mole ratios of MMA and *n*-BuMA units: the cross sections at every 0.02 ppm covering the respective peak areas were accumulated and normalized. The results are shown in Figure 3-1. Thus, the copolymer composition can be directly determined from the elution curves A and B at any specified region in the chromatogram. This is one of the great advantages of this on-line GPC/NMR system over dual detection systems such as UV-RI detectors, which require calibration of the detected intensity for the real chemical composition. The ratio of the areas under the elution curves A and B (33.6 : 66.4) agreed well with the mole ratio of MMA and *n*-BuMA units in the block

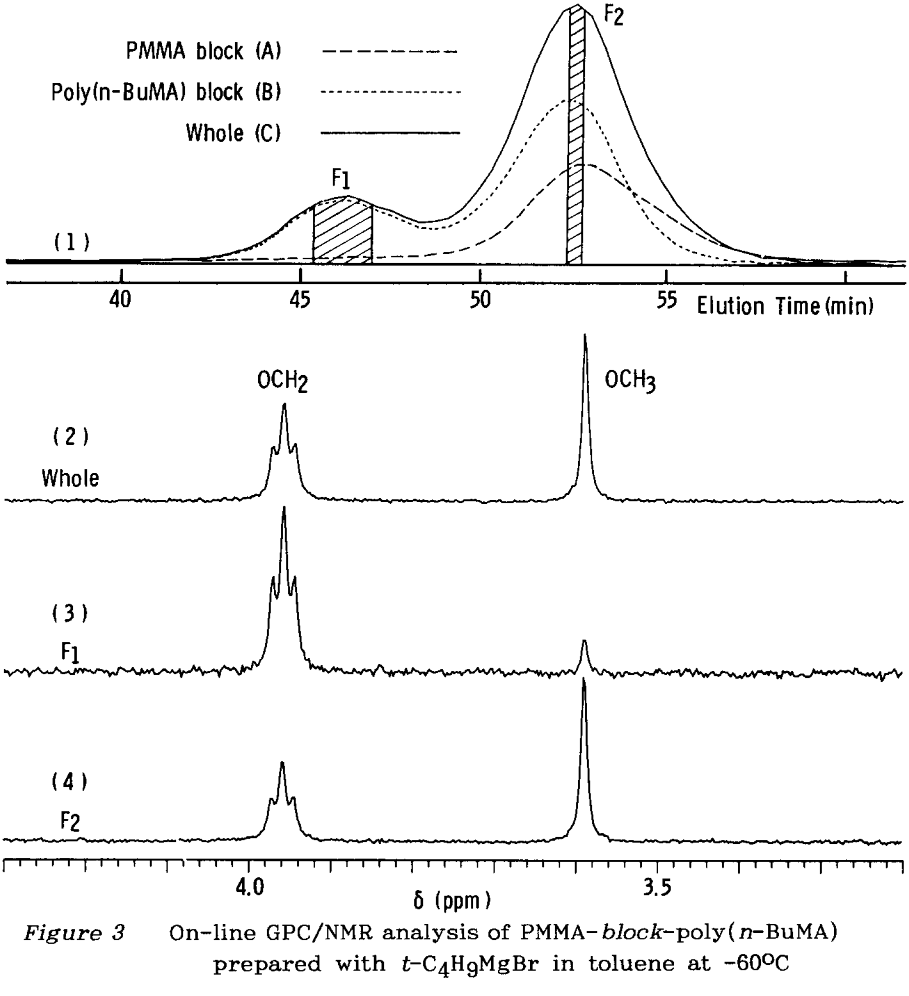

*Figure 3* On-line GPC/NMR analysis of PMMA-*block*-poly(*n*-BuMA) prepared with *t*-$C_4H_9MgBr$ in toluene at -60°C

copolymer (34.3 : 65.7) as determined from the $^1$H NMR spectrum measured under the static conditions (Figure 1-A). The chromatogram C(Figure 3-1C) obtained by summation of the two chromatograms A and B coincided well with that obtained with RI detection. Figure 3 also illustrates the $^1$H NMR spectra ($OCH_3$ and $OCH_2$ region) obtained by summation of all the data blocks covering the whole elution peak (Figure 3-2) and by summation of the data blocks included in the parts of $F_1$ (Figure 3-3) and $F_2$ (Figure 3-4), both indicated in Figure 3-1. The total mole ratio of MMA and *n*-BuMA determined from Figure 3-2 was again 34.5 : 65.5. The results depicted in Figure 3 clearly show that the high molecular weight fraction is rich in *n*-BuMA units, while the low molecular weight fraction is rich in MMA units.

The GPC/NMR data of the PMMA-*block*-poly(*n*-BuMA) was divided into seven regions as indicated in Figure 4. The Mn for each region was calculated from the calibration curve made by using standard polystyrenes, and the chemical composition of each region was determined from the $^1$H NMR spectrum for the region. Degrees of polymerization (DP's) of the PMMA and poly(*n*-BuMA) blocks could be calculated from the Mn's and the chemical compositions for the individual regions. Figure 4 shows the plots of the logarithmic DP of the PMMA and poly(*n*-BuMA) blocks for each region against the molecular weight of the copolymer. The average DP of PMMA blocks was about 30, which corresponds to the $[MMA]_0/[t\text{-}C_4H_9MgBr]_0$ ratio in the polymerization. From the weight fraction and Mn of each region, the Mw/Mn

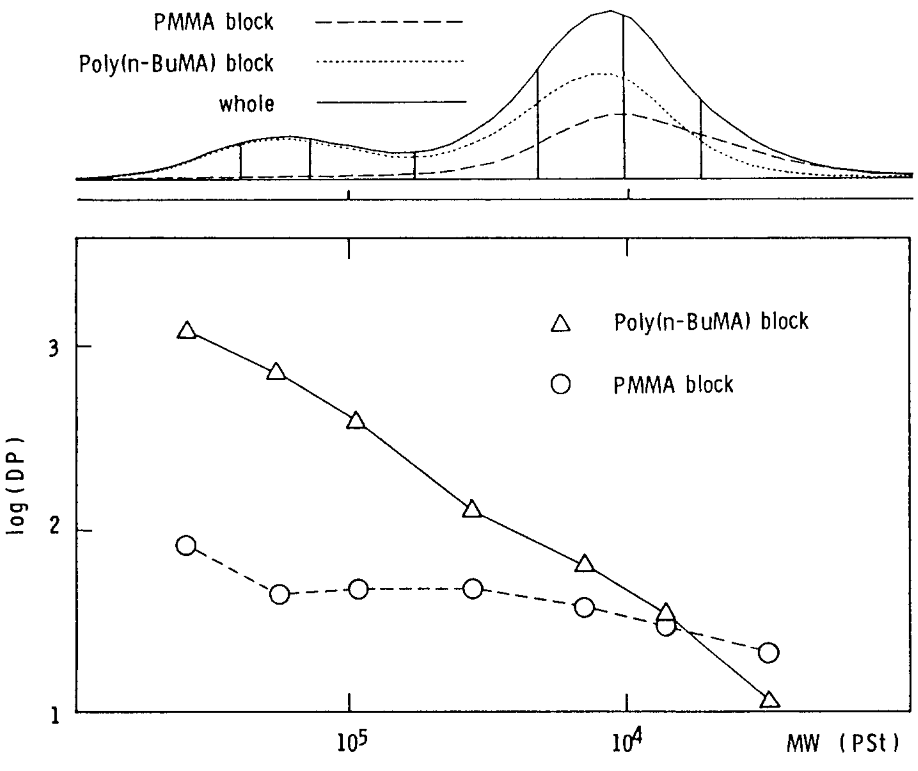

*Figure 4* Plots of DP's of PMMA and poly(*n*-BuMA) blocks in the PMMA-*block*-poly(*n*-BuMA) against molecular weight of the block copolymer

was roughly estimated to be 1.07. The value is close to that for the PMMA homopolymerized with *t*-$C_4H_9MgBr$ in toluene at -60°C. The DP of the PMMA block slightly increases with an increase in the molecular weight of the block copolymer. The result may suggest that the living PMMA anions with higher DP have higher reactivity than those with lower DP in the polymerization of *n*-BuMA. It is also noticeable that the chromatogram showed no detectable peak due to the PMMA homopolymer with DP of 30. On the other hand, log(DP) of poly(*n*-BuMA) block increased linearly with an increase in the Mn of the copolymer. These results show that the polymer is truly a block copolymer formed from the living PMMA anion. The bimodal MWD of the block copolymer indicates that at least two types of active species with different activity should be generated in the polymerization of *n*-BuMA with the living PMMA anion, although the initiation reaction occurred quantitatively. Mn, Mw/Mn and the number of polymer molecule for the high and low molecular weight peaks in the bimodal GPC curve were estimated separately and listed in Table 2. The number of polymer molecules of the high molecular weight fraction was one-fiftieth as much as that of the low molecular weight fraction, although the DP of the former fraction was 10 times as large as that of the latter fraction. This means that about 2 % of the living PMMA anions form the propagating species for the high molecular weight fraction, whose activity was about 500 times as high as that for the low molecular weight fraction.

Table 2 The Number of Polymer Molecules in the High and Low Molecular Weight Fractions of Poly(MMA)-*block*-poly(*n*-BuMA)

| Fraction | Mn (GPC) | $\frac{Mw}{Mn}$ | Number of polymer molecules (mmol) |
|---|---|---|---|
| High MW part | 87800 | 1.19 | 0.028 |
| Low MW part | 9140 | 1.32 | 1.35 |

Polymerization of MMA with *t*-$C_4H_9MgBr$ in toluene at low temperature gave highly isotactic PMMA with narrow MWD, while polymerization of *n*-BuMA gave highly isotactic poly(*n*-BuMA) but with multimodal MWD. Figure 5 shows the results obtained by GPC/NMR experiment on the random copolymer of MMA and *n*-BuMA (MMA/*n*-BuMA = 66.3/33.7) prepared with *t*-$C_4H_9MgBr$ in toluene at -78°C. The chromatogram (Figure 5-1F) clearly shows multimodal MWD. The chromatograms D and E, based on MMA and *n*-BuMA units, respectively, indicate that the chemical composition is almost independent of its molecular weight. Figures 5-2 and 5-3 are the $^1H$ NMR spectra of fractions $F_3$ and $F_4$ indicated in the chromatogram, respectively. It is evident from the spectra that both the fractions are highly isotactic. These results suggest that multiple active species with different reactivities exist in the copolymerization system, but their monomer selectivities and stereoregularities are almost the same.

The present studies clearly show that the on-line GPC/NMR allows us to investigate the molecular weight dependence of the chemical composition of copolymer, in a short time ($\leq$ 60 min), with a small amount of sample($\leq$ 1mg) without calibration, and to extract a wide variety of information from the data of a single experiment. The results obtained by this method will serve to investigate copolymerization mechanism. It is easy to imagine that the application of the GPC/NMR method is not restricted to the analysis of the chemical composition of binary copolymer but can be extended to the analysis of terpolymer or the higher order of multicomponent copolymers as well as the analysis of stereosequence distribution of tactic polymers.

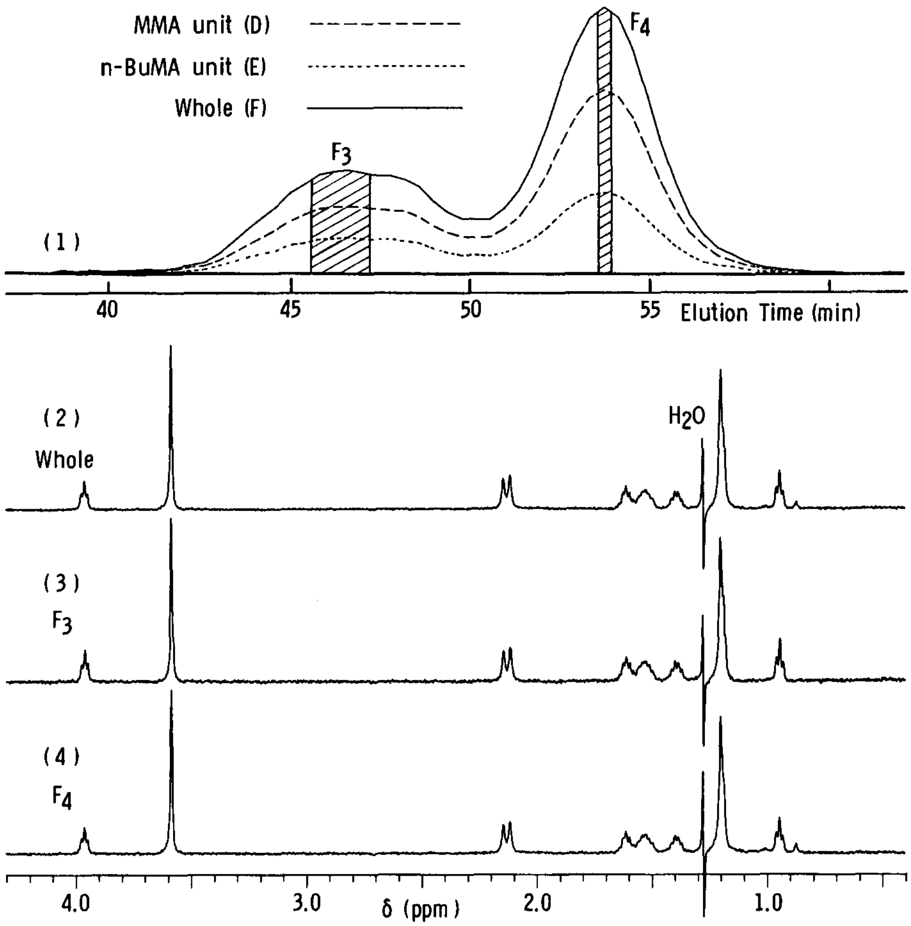

*Figure 5* On-line GPC/NMR analysis of poly(MMA-*ran*-*n*-BuMA) prepared with *t*-$C_4H_9MgBr$ in toluene at -78°C

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Accepted April 17, 1989 S