

**Determination of Monomer Reactivity Ratios from a Single Sample using
Multivariate Analysis of the ^1H NMR Spectra of Poly[(methyl methacrylate)-*co*-
(benzyl methacrylate)]**

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Abstract

Copolymers of methyl methacrylate (MMA) and benzyl methacrylate (BnMA) were prepared by conventional radical copolymerization in toluene at 70 °C. The ^1H nuclear magnetic resonance (NMR) spectra of these copolymers were measured in various solvents at different temperatures. The signals of the methoxy protons in the MMA units and the benzyl protons in the BnMA units showed splitting mainly because of the triad monomer sequences when the temperature was increased to 150 °C in deuterated dimethyl sulfoxide. However, the splitting was not sufficient to determine the mole ratios of the triad sequences. Therefore, multivariate analysis was applied to the ^1H NMR spectra of copolymers with various chemical compositions. Principal component analysis successfully extracted information on the polymer microstructures. Partial least-squares (PLS) regression successfully predicted the mole fractions of the diad monomer sequences. Then, the fractions of the diad sequences in an unknown sample prepared in benzene at 60 °C were predicted using PLS regression to determine the monomer reactivity ratios. Thus, the monomer reactivity ratios were successfully determined from a single sample using multivariate analysis of the ^1H NMR spectra of copolymers of MMA and BnMA.

Keywords: monomer reactivity ratios / chemometrics / NMR / principal component analysis / partial least-squares regression

INTRODUCTION

The free radical copolymerization of two monomers is usually described in terms of the monomer reactivity ratios. For example, in the copolymerization of M_1 and M_2 , the monomer reactivity ratios (r_1 and r_2) are defined as follows:

$$r_1 = k_{11}/k_{12}$$

$$r_2 = k_{22}/k_{21}$$

where k_{ij} denotes the rate constant for the reaction of the M_i -ended radical adding the M_j monomer (i and/or $j = 1$ and/or 2). To determine the monomer reactivity ratios, many experimental methods, such as the intersection method (Mayo-Lewis method),¹ Fineman-Ross method,² nonlinear least-squares fitting method,^{3,4} and Kelen-Tüdös method,⁵ have been developed and are widely used. In these methods, however, the monomer reactivity ratios are estimated by plotting a large amount of data from samples obtained at low conversions with different monomer feed ratios. Therefore, repeated experiments are required when the monomer reactivity ratios are dependent on the polymerization conditions, such as the solvent and temperature.

The monomer reactivity ratios can be determined from a single copolymer at low conversion if the distribution of the monomer sequences is known.⁶⁻¹² For example, the r_1 and r_2 values in the terminal model are determined from the mole fractions of the diad sequences, and the r_{11} , r_{12} , r_{21} , and r_{22} values in the penultimate model are determined from the triad sequences. It is, however, generally difficult to determine quantitatively the mole fractions of the monomer sequences. Therefore, the development of a facile method to determine the mole fractions of monomer sequences is desirable.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the microstructural characterization of polymers. In particular, solution-state NMR is used for analyzing polymer microstructures, including the stereochemistry and the monomer sequences.^{13,14} In addition,¹³C NMR spectra are often used to investigate the stereochemical and monomer-sequence distributions of polymers; this is because ¹³C NMR signals are simplified by ¹H-decoupling and have a wider spectral width than ¹H NMR spectra. The distributions of the monomer sequences have been determined for copolymers composed of combinations of two monomers having quite different structures, such as methyl methacrylate (MMA)-acrylonitrile,¹⁰ vinylidene cyanide-vinyl acetate,¹² vinyl alcohol-vinyl acetate,¹⁵ vinylidene chloride-methyl acrylate,¹⁶ and vinylidene chloride-acrylonitrile.¹⁷ However, complicated spectra are usually observed for copolymers composed of combinations of two monomers with the same parent structure, such as methacrylates, because of the combined stereochemical and monomer-sequence distribution effects. As a result, chemical shifts can be assigned for the monomer sequences, but the distributions of the monomer sequences cannot be determined quantitatively,¹⁸ except for copolymers with highly stereocontrolled structures.¹⁹

Recently, we have reported that the stereochemical distribution in poly(*N*-vinyl-2-pyrrolidone) can be determined from the ¹H NMR signals of the methylene groups adjacent to the C=O groups, which are three bond lengths from the stereogenic centers.²⁰ The experimental conditions, such as the solvent and temperature, had a large effect on the spectral patterns. The most obvious three-line splitting caused by the triad

tacticity was observed in D₂O at 25 °C. An increase in the temperature gradually reduced the splitting, and a broad almost non-split peak was observed at 250 °C. These results suggested that the stereochemical effects on the ¹H NMR signals of the methylene groups far removed from the stereogenic center can be removed by increasing the measurement temperature.

In this study, we attempted to selectively extract monomer sequence information from the ¹H NMR spectra of copolymers. Copolymers of MMA and benzyl methacrylate (BnMA) were selected for the following reasons (Figure 1):

1. the singlet signals of the methoxy protons in the MMA units and the benzyl protons in the BnMA units are observed at different chemical shifts;
2. the effect of tacticity is expected to be reduced by increasing the temperature because both the methoxy and benzyl groups are three bond lengths from the stereogenic centers; and
3. the ring-current effect of the phenyl rings in the BnMA units is expected to enhance the splitting caused by differences in the monomer sequences.

<Figure 1>

The signals of the methoxy and benzyl protons were able to be assigned to the triad sequences under the optimized conditions, but the fractions of the monomer sequences were unable to be determined because of overlapping signals. Therefore, we applied multivariate analysis to the ¹H NMR spectra to predict the distributions of the

diad sequences because multivariate analysis of NMR spectra has been found to be useful for the structural analysis of synthetic (co)polymers.²¹⁻²⁵ Multivariate analysis of the ¹H NMR spectra of copolymers of MMA and BnMA was used to successfully determine the monomer reactivity ratios from a single sample.

EXPERIMENTAL

Materials

MMA and BnMA (supplied by Mitsubishi Chemical Corporation, Otake, Japan) was distilled under reduced pressure. AIBN (2,2'-Azobisisobutyronitrile) (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) was recrystallized from methanol. Toluene (Kanto Chemical Co., Inc., Tokyo, Japan) was purified by washing with sulfuric acid, water, and 5% aqueous sodium hydroxide solution, followed by fractional distillation.

Copolymerization

A mixture of monomer and AIBN were dissolved in toluene to final concentrations of 1.0 and 5.0×10^{-3} mol/L, respectively. The solutions were degassed by several freeze–pump–thaw cycles. The monomer solution was kept at 70 °C under a nitrogen atmosphere. The polymerization was initiated by adding the initiator solution. After 15 min, the polymerization mixture was cooled to room temperature and poured into a large volume of methanol. The polymer precipitate was collected by centrifugation and dried *in vacuo*. The copolymer yield was determined gravimetrically.

Measurements

The molecular weights and molecular weight distributions of the polymers were determined by size-exclusion chromatography (SEC); the chromatograph was calibrated with standard poly(methyl methacrylate) (PMMA) samples. SEC was performed on an HLC 8220 chromatograph (Tosoh Corp., Tokyo, Japan) equipped with TSKgel columns [SuperHM-M (6.5 mm inner diameter \times 150 mm) and SuperHM-H (6.5 mm inner diameter \times 150 mm)] (Tosoh Corp.). *N,N*-Dimethylformamide (DMF) containing 10 mmol \cdot L $^{-1}$ LiBr was used as the eluent at a flow rate of 0.35 mL \cdot min $^{-1}$ at 40 °C. The initial polymer concentration was set at 1.0 mg \cdot mL $^{-1}$.

The ^1H NMR spectra of the copolymers were measured on an ECA500 spectrometer (JEOL Ltd., Tokyo, Japan) equipped with a 5-mm multinuclear probe (^1H : 45° pulse (6.5 μs), pulse repetition 8.49 s, 256 scans). Each ^1H NMR spectrum was stored as 32768 complex data points covering a spectral width of 9384 Hz. A trapezoidal function of 0%, 0%, 40%, and 50%, an exponential function of 0.2 Hz, and zero-fill to 131072 points were applied prior to Fourier transformation (digital resolution = 0.0715 Hz). The ^1H NMR chemical shifts were referenced to internal tetramethylsilane ($\delta = 0.0$ ppm). The chemical composition was determined from the integral intensities of the ^1H NMR signals of the ester groups of the MMA and BnMA units.

Bucket integration at an interval of 0.02 ppm was performed with JEOL Delta NMR ver.5.2 software for the resonance regions of the methoxy protons in the MMA units (3.35–3.65 ppm) and the benzyl protons in the BnMA units (4.80–5.16 ppm). Principal component analysis (PCA) of the obtained data sets was carried out using

python 3.8.5. Partial least-squares (PLS) regression of the data sets of the spectral matrix and the diad-fraction data matrix was conducted using R software ver.3.4.4 with Visual R Platform ver. 2.0 (NTT DATA Mathematical Systems Inc., Tokyo, Japan). The data sets were subjected to leave-one-out cross validations, followed by PLS-2 analysis, in which the fractions of the diad sequences were simultaneously predicted.

RESULTS AND DISCUSSION

¹H NMR measurements of copolymers of MMA and BnMA in various solvents at different temperatures

To examine the effects of solvent and temperature on the ¹H NMR spectra of copolymers of MMA and BnMA, three copolymers with different chemical compositions were prepared by radical copolymerization of MMA and BnMA with AIBN in toluene at 70 °C for 24 h (Table 1). Figure 2 shows the expanded ¹H NMR spectra of the methoxy protons in the MMA units and the benzyl protons in the BnMA units in the copolymer with a MMA content (F_M) of 48.2 mol%, measured in various solvents (2.0 wt%) at different temperatures. Overlapped and broadened signals were observed in CDCl₃ and in some aromatic solvents, including nitrobenzene-*d*₅ and pyridine-*d*₅. However, split signals were observed in benzene-*d*₆ and in toluene-*d*₈. In particular, three discrete signals were observed in benzene-*d*₆. Therefore, the ¹H NMR spectra of copolymers with different F_M values were measured in benzene-*d*₆ at 60 °C (Figure S1). Although the F_M values were varied from 29.9 mol% to 67.2 mol%, the spectral pattern of the methoxy and benzyl protons was maintained. This result indicated that the splitting of signals observed in

benzene- d_6 reflected differences in the stereosequences rather than in the monomer sequences.¹⁴

<Table 1>

<Figure 2>

Broad but shouldered signals were observed in polar solvents, including deuterated dimethyl sulfoxide (DMSO- d_6) and DMF- d_7 . In particular, the signals observed in DMSO- d_6 appeared to reflect different monomer sequences. Therefore, the ^1H NMR spectra of copolymers with different F_M values were measured in DMSO- d_6 at 150 °C (Figure 3). With an increase in the F_M value, the intensity of the lower-field shoulder peak of the methoxy signal increased. In contrast, with a decrease in the F_M value, the intensity of the higher-field shoulder peak of the benzyl signals increased. These results suggested that the splitting observed in DMSO- d_6 reflected differences in the monomer sequences rather than in the stereosequences. The methoxy signals were assigned as the MMA-centered triad sequences, MMM, MMB, and BMB, whereas the benzyl signals were assigned as the BnMA-centered BBB, MBB, and MBM triads, where the letters M and B denote the MMA and BnMA units, respectively. The splitting of the signals gradually diminished as the temperature was decreased from 150 °C to 25 °C (Figure S2). Therefore, the ^1H NMR signals of copolymers of MMA and BnMA could be assigned to the triad stereosequences by optimizing the measurement conditions, as expected. However, it was difficult to directly determine the triad monomer-sequence

distributions from the ^1H NMR spectra because of the overlapping signals. Therefore, we applied multivariate analysis to the ^1H NMR spectra of copolymers of MMA and BnMA to predict the monomer-sequence distributions.

<Figure 3>

PCA to extract information on the monomer sequences

Eight copolymers with different F_M values were prepared by radical copolymerization of MMA and BnMA in toluene at 70 °C for 15 min (Table 2). The polymer yields were suppressed so as not to exceed 5%. The monomer reactivity ratios for the radical copolymerization of MMA and BnMA in toluene at 70 °C were determined to be $r_M = 0.84$ and $r_{Bn} = 1.26$ by nonlinear least-squares fitting of the Mayo-Lewis terminal model, expressed as Equation (1).^{26,27}

$$F_M = \frac{r_M f_M^2 + f_M f_{Bn}}{r_M f_M^2 + 2 f_M f_{Bn} + r_{Bn} f_{Bn}^2} \quad (1)$$

where f_M and f_{Bn} denote the mole fractions of the MMA and BnMA monomers, respectively, in the feed ($f_M + f_{Bn} = 1$), and r_M and r_{Bn} denote the monomer reactivity ratios (Figure 4). Then, the sequences at the diad level were calculated by Equations (2)–(4).^{22,28}

$$F_{MM} = F_M \left(1 - \frac{2 F_{Bn}}{1 + \sqrt{1 + 4 (r_M r_{Bn} - 1) F_M F_{Bn}}} \right) \quad (2)$$

$$F_{MBn} = \frac{4 F_M F_{Bn}}{1 + \sqrt{1 + 4 (r_M r_{Bn} - 1) F_M F_{Bn}}} \quad (3)$$

$$F_{BnBn} = F_{Bn} \left(1 - \frac{2 F_M}{1 + \sqrt{1 + 4 (r_M r_{Bn} - 1) F_M F_{Bn}}} \right) \quad (4)$$

where F_{Bn} denotes the mole fraction of the BnMA unit in the copolymers ($F_{\text{M}} + F_{\text{Bn}} = 1$), F_{MM} and F_{BnBn} denote the mole fractions of homo diads in the copolymers, and F_{MBn} denotes the mole fraction of hetero diads in the copolymers. The calculated values are summarized in Table 2.

<Figure 4>

PCA was performed on two spectral regions—the methoxy and benzyl signals—in the ^1H NMR spectra of eight copolymers obtained in the early stages of polymerization. Two types of datasets were used for the analyses: the sum of the integral intensities of the methoxy and benzyl signals was normalized to be 100 (Dataset **A**), and each sum of the integral intensities of the methoxy and benzyl signals was individually normalized to be 100 (Dataset **B**).

Figure 5 shows the PCA score plots for the two types of datasets. Similar contribution rates of variances for the first (PC1) and second (PC2) principal components were observed (Dataset **A**: PC1 63.8% and PC2 26.9%; Dataset **B**: PC1 64.9% and PC2 27.1%). Thus, the first two principal component factors accounted for 90.7% and 92.0% of the spectral information of Datasets **A** and **B**, respectively. Inverted parabolic relationships were obtained regardless of the type of dataset used. The PC1 score increased with an increase in the F_{M} value, whereas the PC2 score decreased with an increase in the fraction of hetero diads, F_{MBn} . It was therefore assumed that the PC1 and PC2 values reflected mainly the chemical composition and the monomer sequence,

respectively. Similar results have been observed for PCA of the ^{13}C NMR spectra of the copolymers of methacrylate monomers.^{22,24,25}

<Figure 5>

Figure 6 shows the PCA loading plots obtained with Dataset **A**, which contain information on the spectral variations of the original dataset. The corresponding ^1H NMR spectra of the copolymers with different F_M values are also shown. Positive PC1 loadings were observed in the region corresponding to symmetrical MMA-rich triads, particularly the MMM triad, whereas negative PC1 loadings were observed in the region corresponding to symmetrical BnMA-rich triads, particularly the BBB triad. Positive PC2 loadings were observed in the regions corresponding to symmetrical triads, whereas negative PC2 loadings were observed for asymmetrical triads, the MMB and MBB triads. These results also suggested that the PC1 and PC2 values reflected mainly the chemical composition and monomer sequence, respectively.

<Figure 6>

Dataset **B** gave loading plots that extracted better information on the monomer sequences than the plots using Dataset **A** (Figure 7). Positive PC1 loadings were clearly observed in the regions corresponding to the MMM and MBM triads, whereas negative PC1 loadings were clearly observed in the regions corresponding to the BBB and BMB

triads. Positive PC2 loadings were observed in the regions corresponding to the symmetrical triads, MMM, BMB, BBB, and MBM, whereas negative PC2 loadings were observed for the asymmetrical triads, MMB and MBB. Thus, Dataset **B** was preferable to Dataset **A** for the extraction of information on the monomer sequences.

<Figure 7>

PLS regression to predict the fractions of diad sequences

PLS regression was applied to the Datasets **A** and **B** to predict the monomer-sequence distribution. For calibration, the theoretical fractions of the diad sequences, F_{MM} , F_{MBn} , and F_{BnBn} (Table 2) were used. To determine the number of latent variables in the PLS model, leave-one-out cross-validation was conducted. The cross-validated coefficient of determination (r^2_{CV}) was calculated from Equation (5):

$$r^2_{CV} = 1 - \frac{\sum_i (y_i - y_{i_{CV}})^2}{\sum_i (y_i - y_{i_A})^2} \quad (5)$$

where y_i , $y_{i_{CV}}$, and y_{i_A} denote the theoretical diad fraction, the fraction predicted by leave-one-out cross-validation, and the averaged diad fraction of the sample i , respectively. The r^2_{CV} values were found to be *ca.* 0.53 with one latent variable, regardless of the dataset used (Figure S3). Obvious deviations were observed particularly for the hetero diad, F_{MBn} . The use of two latent variables obviously improved the r^2_{CV} values, which were 0.876 and 0.859 for Datasets **A** and **B**, respectively. Further increasing the number of latent variables gradually improved the r^2_{CV} values, which were ≥ 0.93 using four latent

variables (Figure 8). Taking into account that only eight samples were used for the cross-validation, this calibration model with four latent variables could reasonably predict the monomer-sequence distribution in the copolymers of MMA and BnMA (Figure 9). Notably, the r^2_{CV} values for Dataset **A** were always slightly higher than those for Dataset **B**.

<Figure 8><Figure 9>

Determination of monomer reactivity ratios from a single sample

Radical copolymerization of equimolar mixtures of MMA and BnMA was carried out in benzene at 60 °C (Table 3). Then, the monomer-sequence distributions in the copolymer were predicted using the PLS models described above. The fractions of diad sequences were predicted to be $F_{MM} = 23.7$ mol%, $F_{MBn} = 48.8$ mol%, and $F_{BnBn} = 27.5$ mol% with Dataset **A**, and $F_{MM} = 24.6$ mol%, $F_{MBn} = 48.3$ mol%, and $F_{BnBn} = 27.1$ mol% with Dataset **B**. Almost the same distributions were predicted regardless of the dataset used. The F_M values were calculated to be 48.1 mol% and 48.7 mol% for Datasets **A** and **B**, respectively, according to the relationship, $F_M = F_{MM} + F_{MBn}/2$. The value obtained with Dataset **A** was closer to the value (47.3 mol%) determined from the ^1H NMR signals (Table 3). This result suggested that Dataset **A** was preferable to Dataset **B** for predicting the distribution of the diad sequences. Dataset **A** gave a better prediction probably because Dataset **B** loses information on the chemical composition by normalizing individually the integral intensities of the methoxy and benzyl signals.

If the mole fractions of diad sequences are obtained for a copolymer obtained at low conversion, the monomer reactivity ratios can be determined by Equations (6) and (7):^{6,8}

$$r_M = \frac{f_{Bn}}{f_M} \frac{2 F_{MM}}{F_{MBn}} \quad (6) \qquad r_{Bn} = \frac{f_M}{f_{Bn}} \frac{2 F_{BnBn}}{F_{MBn}} \quad (7)$$

Therefore, using the predicted fractions of the diad sequences, the monomer reactivity ratios were calculated to be $r_M = 0.97$ and $r_{Bn} = 1.13$ with Dataset **A** and $r_M = 1.02$ and $r_{Bn} = 1.12$ with Dataset **B**. Both the r_M and r_{Bn} values calculated with Dataset **B** exceeded unity, which is improbable in a radical copolymerization. The r_M and r_{Bn} values calculated with Dataset **A** were comparable to the literature values for the radical copolymerization of MMA and BnMA in benzene at 60 °C ($r_M = 0.85$ and $r_{Bn} = 1.14$, determined by the intersection method).²⁹ These results suggested again that Dataset **A** is preferable to Dataset **B** to predict the distribution of diad sequences, and indicated that the monomer reactivity ratios can be successfully determined from a single sample with probable accuracy using the diad fractions predicted with Dataset **A**.

The solvent effect on the monomer reactivity ratios has been investigated.^{30,31} For example, when the radical copolymerization of styrene (M_1) with MMA (M_2) was conducted in benzonitrile instead of benzene, the r_1 value decreased (0.57 to 0.48) and the r_2 value increased (0.46 to 0.49).³² Similar results have been observed for the copolymerization of styrene (M_1) and butyl acrylate (M_2) (r_1 : 0.84 to 0.73, r_2 : 0.18 to 0.33).³³ These results indicated that the solvent polarity considerably affected the monomer reactivity ratios, at least in copolymerization systems of non-polar and electron-

donating monomers, such as styrene, with polar and electron-withdrawing monomers, such as (meth)acrylates. Therefore, the radical copolymerization of MMA and BnMA was conducted in benzonitrile at 60 °C (Table 3). The monomer reactivity ratios were calculated to be $r_M = 0.96$ and $r_{Bn} = 1.06$ using the diad fractions predicted with Dataset A. Both the r_M and r_{Bn} values were slightly reduced on changing the solvent from benzene to benzonitrile. In addition, the differences between the r_M and r_{Bn} values calculated for the copolymers obtained in benzene and benzonitrile were smaller than those for styrene-containing copolymerization systems. It was therefore assumed that the solvent effect on the radical copolymerization is only slight in systems composed of polar and electron-withdrawing monomers having the same parent structure compared with those composed of non-polar and electron-donating monomers with polar and electron-withdrawing monomers.

CONCLUSIONS

Copolymers of MMA and BnMA were prepared by conventional radical copolymerization. The NMR signals of the methoxy and benzyl protons showed splitting mainly because of differences in the monomer sequences when the temperature was increased to 150 °C in DMSO- d_6 . The signals could be assigned to the triad sequences, but the splitting was insufficient to determine the mole fractions of the triad sequences. Therefore, multivariate analysis was applied to the ^1H NMR spectra of copolymers with various chemical compositions. PCA was conducted with the bucket integral intensities for the methoxy and benzyl signals in the ^1H NMR spectra. The PC1 and PC2 successfully

extracted mainly information on the chemical composition and monomer sequence, respectively. Then, PLS regression was conducted with the datasets as explanatory variables and the theoretical diad fractions as target variables. A satisfactory calibration model was constructed using four latent variables. Therefore, PLS regression was applied to an unknown sample to predict the mole fractions of the diad sequences, which were used to calculate the monomer reactivity ratios. The calculated monomer reactivity ratios were consistent with the literature values. Thus, the monomer reactivity ratios were successfully determined from a single sample using multivariate analysis of the ^1H NMR spectra of copolymers of MMA and BnMA. Furthermore, the method proposed in this study is expected to be extended to the penultimate model to determine the r_{11} , r_{12} , r_{21} , and r_{22} values, if the distribution of triad sequences is given.

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Supplementary Information accompanying this paper can be found on the Polymer Journal website (<http://www.nature.com/pj>).

Table 1. Radical polymerization of MMA and BnMA in toluene at 70 °C for 24 h.^a

MMA / mol%		Yield / %	M_n^c $\times 10^{-4}$	M_w/M_n^c
in feed (f_M)	in copolymer ^b (F_M)			
30.0	29.9	90	3.9	2.5
50.0	48.2	84	8.6	2.7
70.0	67.2	87	4.4	2.7

^a $[MMA]_0 + [BnMA]_0 = 1.0$ mol/L, $[AIBN]_0 = 5.0 \times 10^{-3}$ mol/L.

^b Determined from the 1H NMR signal intensities of the $-OCH_3$ and $-OCH_2Ph$ protons.

^c Determined by SEC (PMMA standards).

Table 2. Radical polymerization of MMA and BnMA in toluene at 70 °C for 15 min.^a

Code	MMA / mol%		Yield / %	M_n^c $\times 10^{-4}$	M_w/M_n^c	Diad / mol% ^d		
	in feed (f_M)	in copolymer ^b (F_M)				F_{MM}	F_{MBn}	F_{BnBn}
M-8	10.1	7.6	3.2	3.2	4.1	0.6	14.0	85.4
M-27	30.1	26.9	1.4	4.6	3.2	7.5	38.9	53.6
M-34	40.6	33.8	2.7	2.7	2.7	11.7	44.2	44.1
M-46	50.0	45.6	5.0	3.3	2.4	21.2	48.9	29.9
M-56	60.1	55.8	3.5	2.9	1.9	31.5	48.6	19.9
M-66	70.1	66.4	2.5	2.2	2.2	44.4	44.0	11.6
M-76	79.9	75.9	2.1	3.0	2.1	57.8	36.2	6.0
M-88	90.0	88.2	2.9	2.7	1.6	77.9	20.7	1.4

^a $[MMA]_0 + [BnMA]_0 = 1.0$ mol/L, $[AIBN]_0 = 5.0 \times 10^{-3}$ mol/L.

^b Determined from the 1H NMR signal intensities of the $-OCH_3$ and $-OCH_2Ph$ protons.

^c Determined by SEC (PMMA standards).

^d Calculated from Equations (2)–(4).

Table 3. Radical polymerization of MMA and BnMA at 60 °C.^a

Solvent	MMA / mol%		Time / h	Yield / %	M_n^c $\times 10^{-4}$	M_w/M_n^c
	in feed (f_M)	in copolymer ^b (F_M)				
benzene	50.0	47.3	1.0	4.4	2.6	1.6
benzonitrile	49.8	46.6	2.0	9.1	4.3	2.0

^a $[MMA]_0 + [BnMA]_0 = 1.0$ mol/L, $[AIBN]_0 = 5.0 \times 10^{-3}$ mol/L.

^b Determined from the ¹H NMR signal intensities of the –OCH₃ and –OCH₂Ph protons.

^c Determined by SEC (PMMA standards).

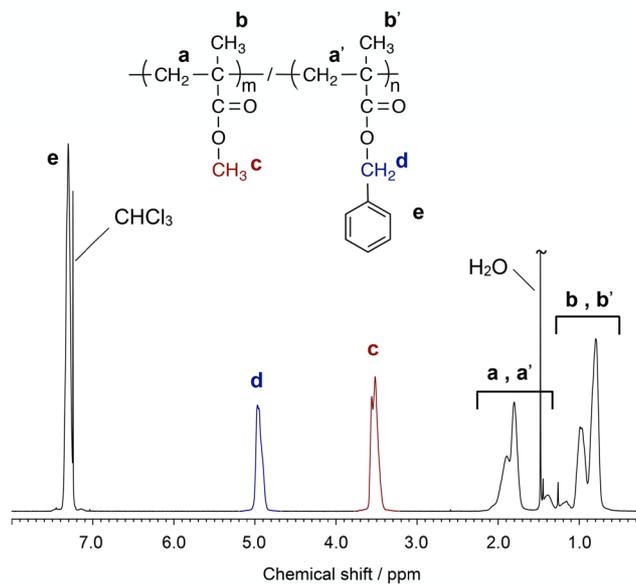


Figure 1 ¹H NMR spectrum of poly(MMA-*co*-BnMA) measured in CDCl₃ at 55 °C.

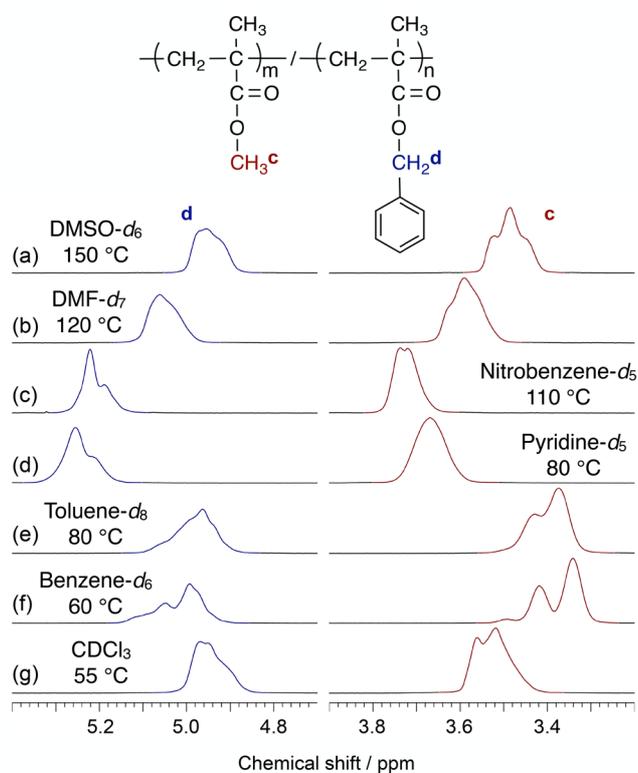


Figure 2. Expanded ^1H NMR spectra of the methoxy protons in the MMA units and the benzyl protons in the BnMA units in the copolymer with an F_M value of 48.2 mol%, measured in (a) DMSO- d_6 at 150 °C, (b) DMF- d_7 at 120 °C, (c) nitrobenzene- d_5 at 110 °C, (d) pyridine- d_5 at 80 °C, (e) toluene- d_8 at 80 °C, (f) benzene- d_6 at 80 °C, and (g) CDCl_3 at 55 °C.

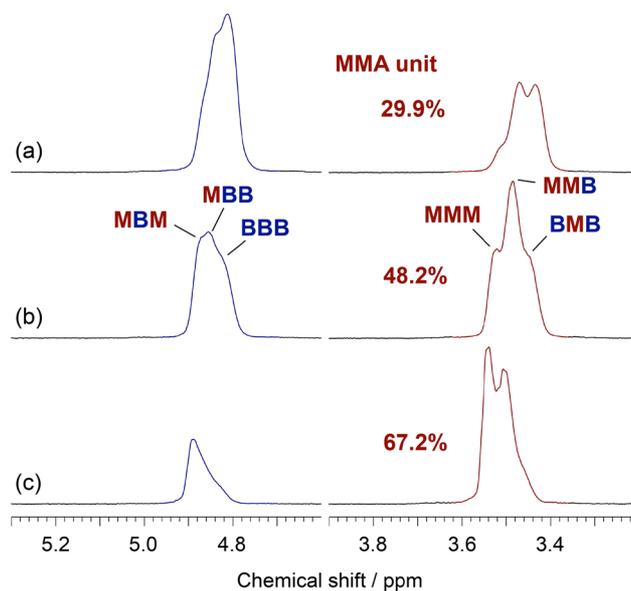


Figure 3 Expanded ¹H NMR spectra of the methoxy protons in the MMA units and the benzyl protons in the BnMA units in copolymers with F_M values of (a) 29.9 mol%, (b) 48.2 mol%, and (c) 67.2 mol%, measured in DMSO- d_6 at 150 °C.

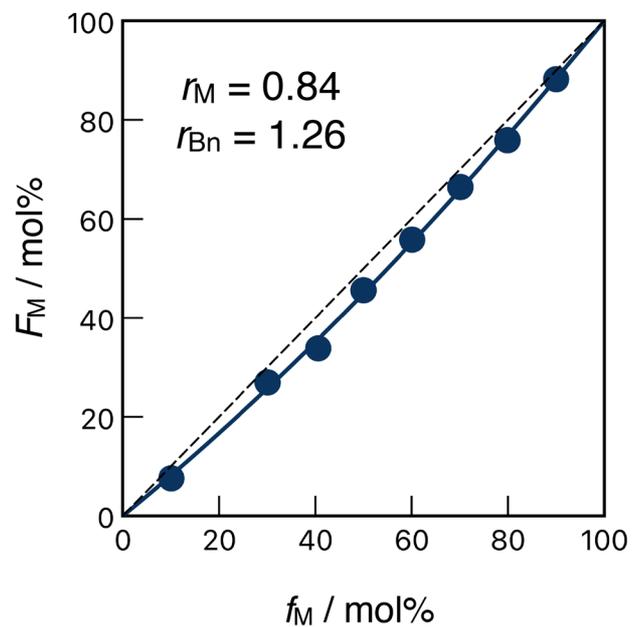


Figure 4. Determination of the monomer reactivity ratios for the radical copolymerization of MMA and BnMA in toluene at 70 °C via the nonlinear least-squares fitting method.

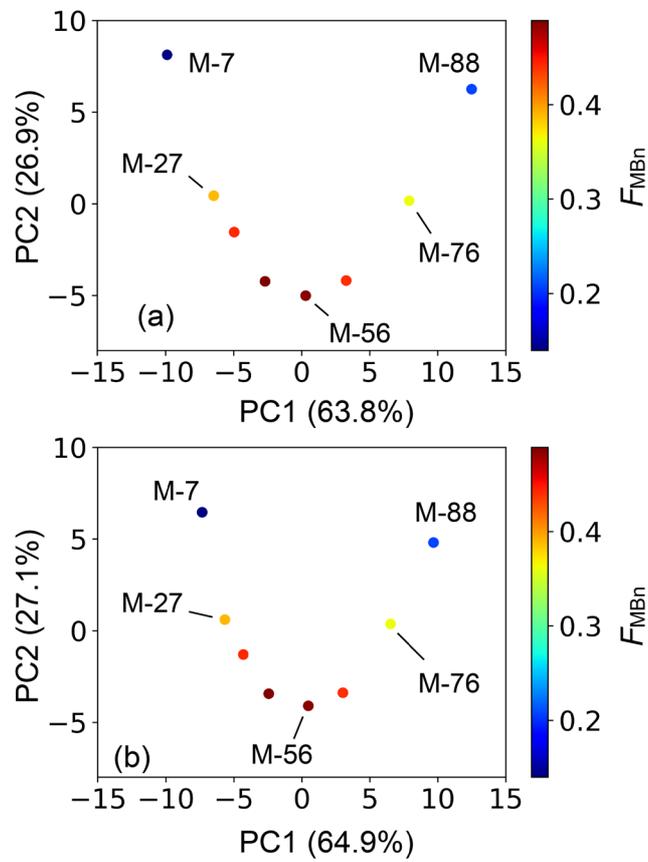


Figure 5. Score plots of the first (PC1) and second (PC2) principal components obtained with (a) Dataset A and (b) Dataset B. The number in parentheses is the contribution rate of variance for each principal component.

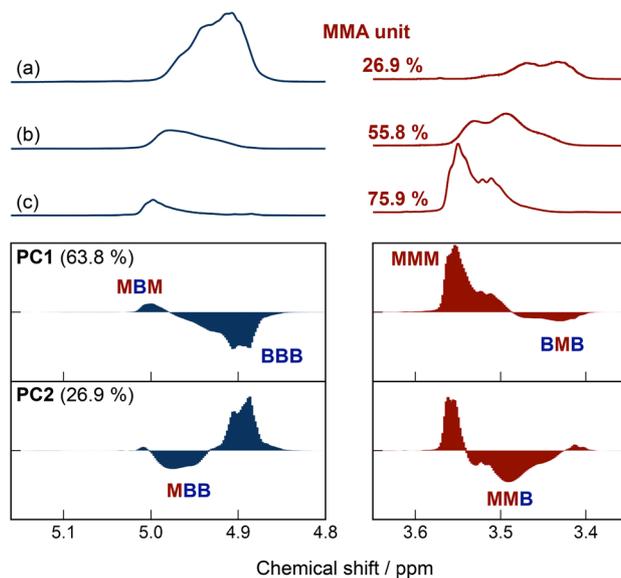


Figure 6 PC1 and PC2 loading plots obtained from Dataset A, with the corresponding ^1H NMR spectra of the benzyl and methoxy protons of the copolymers with F_M values of (a) 26.9 mol%, (b) 55.8 mol%, and (c) 75.9 mol%. The number in parentheses is the contribution rate of variance for each principal component.

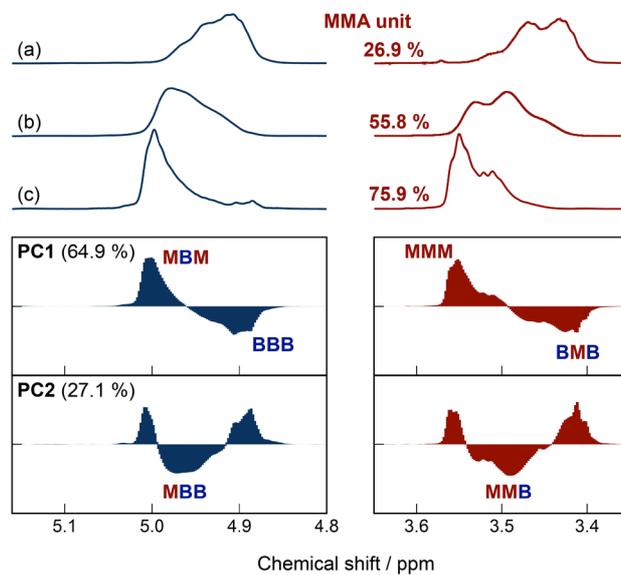


Figure 7 PC1 and PC2 loading plots obtained from Dataset **B**, with the corresponding ¹H NMR spectra of the benzyl and methoxy protons of the copolymers with F_M values of (a) 26.9 mol%, (b) 55.8 mol%, and (c) 75.9 mol%. The number in parentheses is the contribution rate of variance for each principal component.

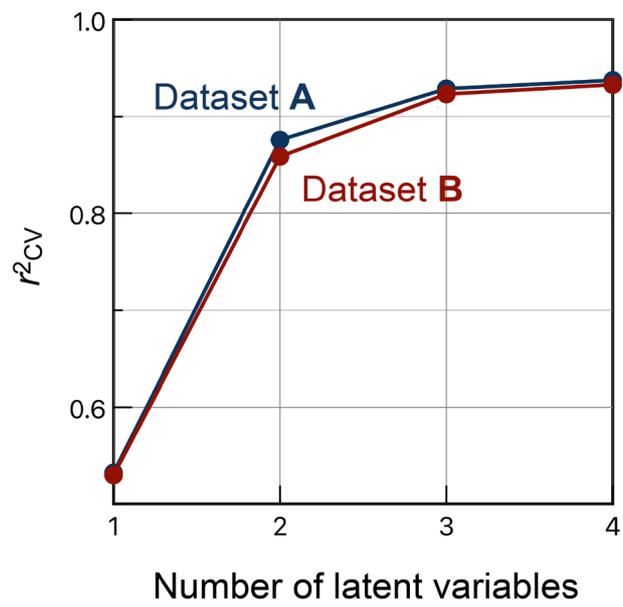


Figure 8 Relationship between the number of latent variables and the r^2_{CV} values.

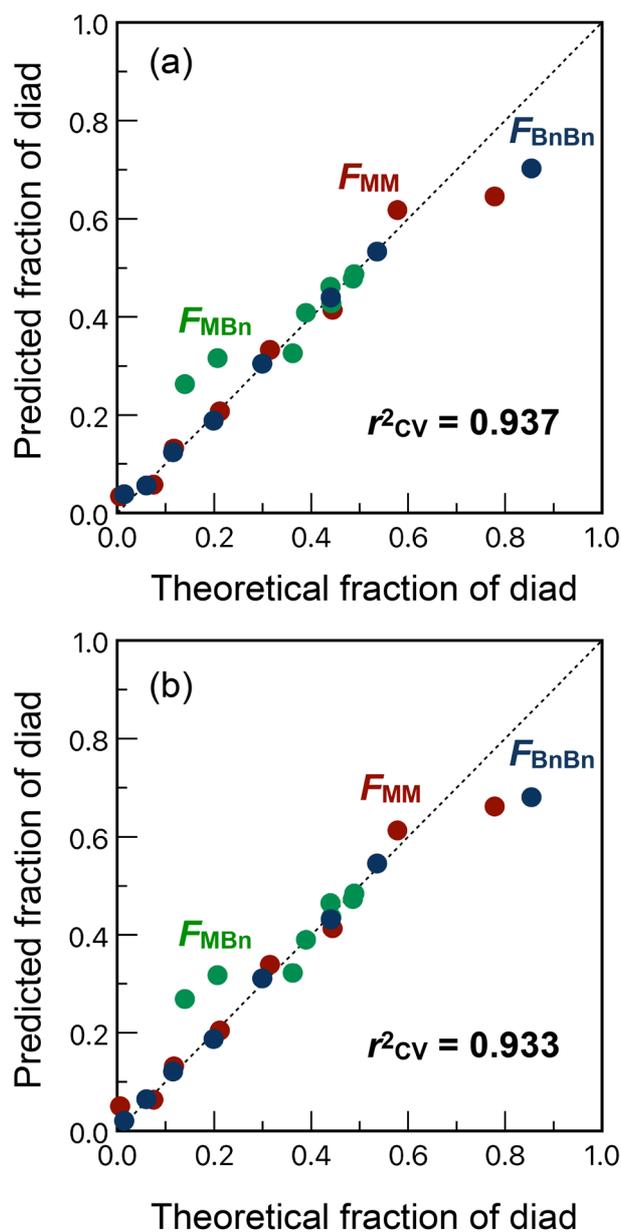


Figure 9 Relationship between the theoretical fractions of the diad sequences with the fractions predicted by leave-one-out cross-validation with four latent variables of (a) Dataset A and (b) Dataset B.