種々の高分子反応で合成したメタクリル酸メチル-メタクリル酸ベンジル共重合体の連鎖解析

Monomer sequence analysis of poly(methyl methacrylate-*co*-benzyl methacrylate)s prepared by various polymer reactions

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ABSTRACT

The analysis of monomer sequences is vital for the improvement of polymeric materials. Here, we performed multivariate analysis on the ^{13}C NMR spectra of methacrylate copolymers synthesized through the partial chemical deprotection of poly(methyl methacrylate-benzyl methacrylate) (poly(MMA-*co*-BnMA)) via six routes to investigate the molecular structures of the resulting polymeric compounds. The benzyl groups were removed from poly(benzyl methacrylate) (PBnMA) through catalytic hydrogenolysis, acidic debenzylation, saponifiaction, and transesterification. The copolymers of BnMA and methacrylic acid (MAa) were converted to poly(MMA-BnMA)s through methylation with diazomethane prior to the analysis. Furthermore, poly(MMA-BnMA)s were obtained from poly(MAa through either benzylation–methylation or methylation–benzylation.

Principal component analysis was performed on the 13C NMR spectra of poly(MMA-BnMA)s containing various ratios of BnMA and MMA units. The results indicated that the monomer sequences of the copolymers synthesized through acidic debenzylation and methylation–benzylation resembled those of radical copolymers (nearly random), whereas the monomer sequences of the copolymers synthesized through catalytic hydrogenolysis resembled the sequences of homopolymer blends (blocky). However, the sequences of the copolymers synthesized through Saponification and transesterification exhibited a relatively alternating tendency. Furthermore, the sequences of the copolymers derived from benzylation–methylation were suggested to exhibit a relatively blocky tendency.

Keywords: Acidic debenzylation, Saponification, Catalytic hydrogenolysis, Transesterification, Principal component analysis

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Chapter 1 Introduction

1.1 General Background Information

The word polymer is derived from the classical Greek words poly meaning many and meres meaning parts. Generally stated, a polymer is made from a long chain molecular that is a large number of repeating units. Obtain polymers with new and desirable properties by linking two or three different monomers or repeating units during the polymerization. Polymers with two different repeating units in their chains are called copolymers. Examples of commercially relevant the most important copolymers are derived from vinyl monomers such as styrene, ethylene, and vinyl chloride.

Recently, a growing tendency of research groups have begun working toward various strategies to control monomer sequence distribution [1-7]. Indeed, polymers with defined macromolecular sequences may exhibit unique conformational and functional properties. For instance, sequence-ordered biopolymers such as nucleic acids and proteins are the keystones of highly organized biological systems. In molecular recognition or intermolecular information transfer between polymer chains, multiple-stranded helices of polymers may provide a very important specific role. Thus, it seems obvious that in molecular recognition or intermolecular information transfer between polymer chains, multiple-stranded helices of polymers may provide a very important specific role.

The properties of polymers are strongly influenced by details of the primary structures that details include the molecular weight, molecular weight distribution, chemical composition and the sequence of monomer units in the case of copolymers, the stereoregularity, end group or branch structure of the chain (Figure 1.1). For example the mechanical properties, chemical properties, and heat resistance increases as molecular weight increases. After that, molecular weight reaches a certain level, the increases rate

will slow down. However, with the enhancement the mechanical properties, the melt viscosity will rise, so that it is not easy to process. Hence, the molecular weight of industrial polymer materials have a certain value, rather than blindly using high molecular weight polymer materials. Additionally, stereoregularity and configutation of monomer chain can affect the properties of polymer because the structure of polymer affects the cohesive energy and crystalline that the thermal and mechanical properties to change. Therefore, how to prepare different primary structure has aroused considerable interest.

Investigation on the primary structure have many methods. For instance, the high resolution nuclear magnetic resonance (NMR) spectroscopy, fourier transform infrared spectroscopy (FT-IR), gas chromatography mass spectroscopy (PyGC-MS), matriz-assisted laser desorption ionization (MALDI) [5],etc. Among them, NMR spectroscopy is allow a relatively precise examination of polymer microstructure. For this purpose, high-resolution NMR spectroscopy is usually the method of choice.

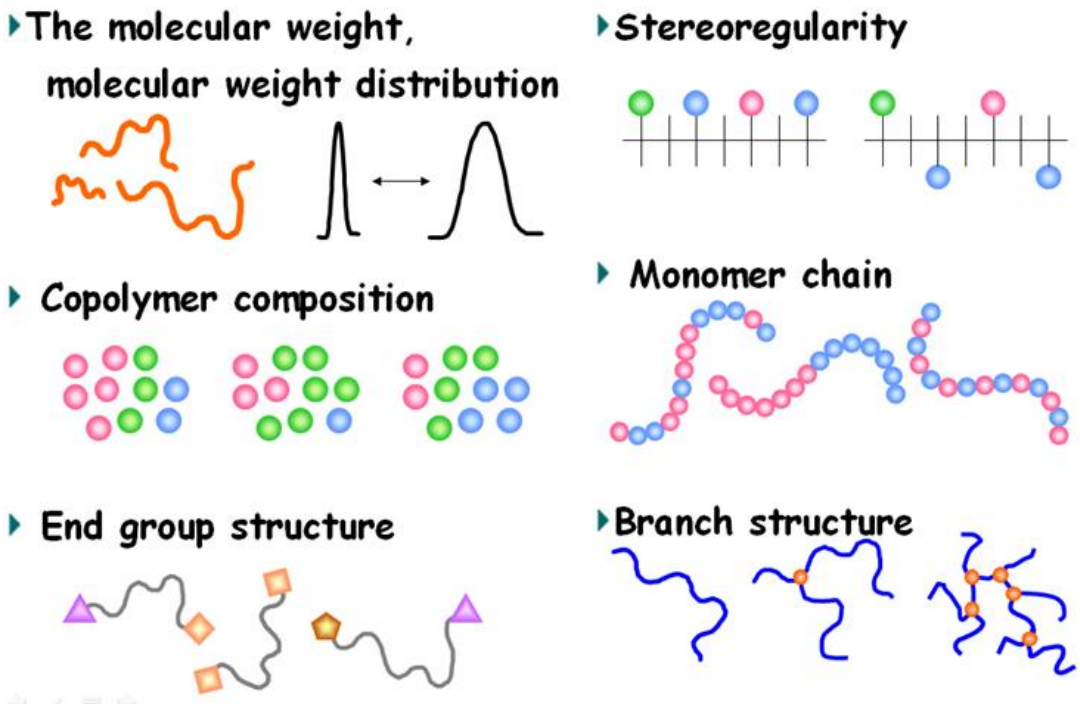


Figure 1.1. Primary structure of polymer

Nevertheless, understanding and controlling are two very different things. Granted that the limitations of the present situation are obvious, concrete options for controlling the primary structure of synthetic polymers are still few. Representative types of interest in copolymerization studies is the styrene-methyl methacrylate (MMA) [8-11]. ^{1}H NMR and ^{13}C NMR spectroscopy indicated that monomer sequence of alternating type in styrene-MMA copolymer. Yet, although very elegant, these kinds of case limited to very different chemical shift of polymers.

Synthetic methods for sequence controlled polymerization are typically obtained by iterative, step growth, chain growth. For synthetic polymers, iterative strategy was studied as early as the late 1940s for the synthesis of oligopeptides. The representative might be iterative exponential growth via stepwise reaction[12-13], which has recently been developed into a semi-automated flow system and enable the synthesis of a large amount of single molecular weight polymers consisting of sequence regulated repeating units, but is unable to produce high molecular weights and is generally time intensive [14-15]. For synthetic polymers, step-growth polymerizations rely on functional monomers containing reactive termini. Step growth polymerizations can be easily transformed into sequence-specific oligomerizations if appropriate protection-deprotection cycles are performed, but lack control over polymer molecular weight and dispersity [16]. For synthetic polymers, chain growth strategies have controlled polymerization characteristics. The growing species in a chain growth polymerization under usual conditions can, by definition, constantly and continuously reacts with monomers, rendering an iterative single monomer propagation(propagation one by one), but lack a high level of sequence precision when compared to the previous methods[17-20].

Much attention has also been directed toward the vinyl copolymers obtained by

polymer reaction (partial modification). Among them, prepared copolymer by polymer reaction and using NMR to extract quantitative information of monomer sequence. The poly(vinyl acetate-vinyl alcohol) (VAc-VOH) which prepared through the alcoholysis or saponification of poly(vinyl acetate)s and by reacetylation of poly(vinyl alchol) have been reported [21-23]. The average sequence length can be calculated from VAc and VOH units based on dyad sequence (Figure 1.2). Kawauchi and coworkers reported synthesized highly stereoregular polymethacrylates by two-step esterification of syndiotactic (96 % in triads) or isotactic (98 % in triads) poly(methacrylic acid) (PMAa) prepared by stereospecific anionic living polymerization[24].Klesper has determined the triad fractions of partially hydrolyzed syndiotactic PMMA samples with 100MHz proton resonance spectra and has shown that the triad fractions are in good agreement with a random hydrolysis model [25-26]. Another example synthesized highly stereoregular polymethacrylates by group transfer polymerization (GTP) of syndiotactic (97.5% in triads) PMMA as determined by 750MHz ^{1}H NMR [27].

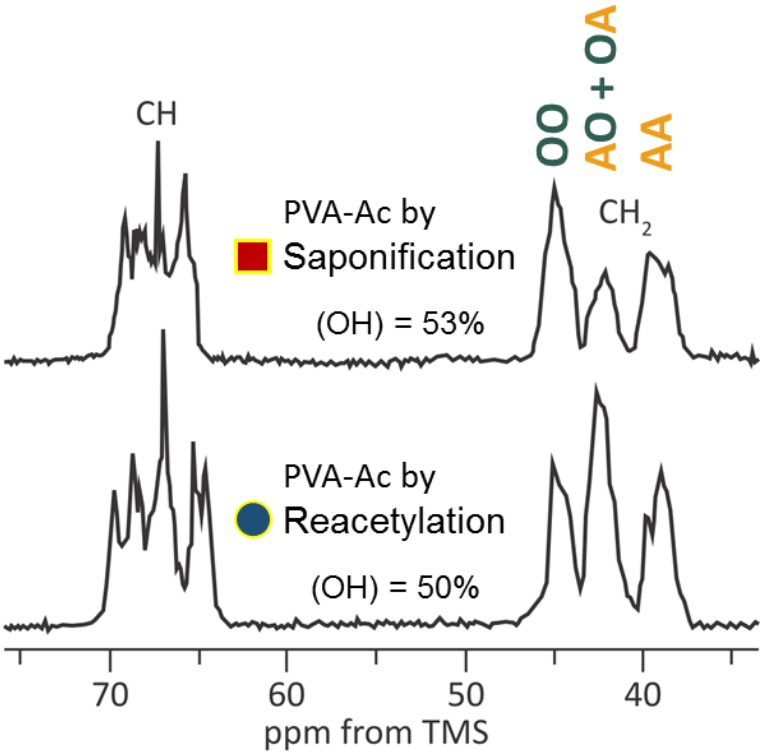


Figure 1.2. 25.1MHz ^{13}C-FT-NMR spectra of two samples of PVA-Ac prepared by direct saponification and by reacetylation. The stick spectrum represents the ^{13}C chemical shift values calculated for the three different sequences.

However, the monomer sequence of atactic copolymers of methacrylates determination were more difficult due to copolymer structure were still perplexing when the chemical shifts of the signals are sensitive to both configurational sequence and monomer sequence. For example, the ^{13}C NMR spectroscopy of stereoregular copolymers of poly(methyl methacrylate-co-butyl methacrylate (Figure 1.3). The copolymer structure would be changed with different ratio of monomer, NMR spectra chemical shifts of the signals thus depended on both configurational sequences and monomer sequences, as reported by T. Nishiura in 2000 [28].

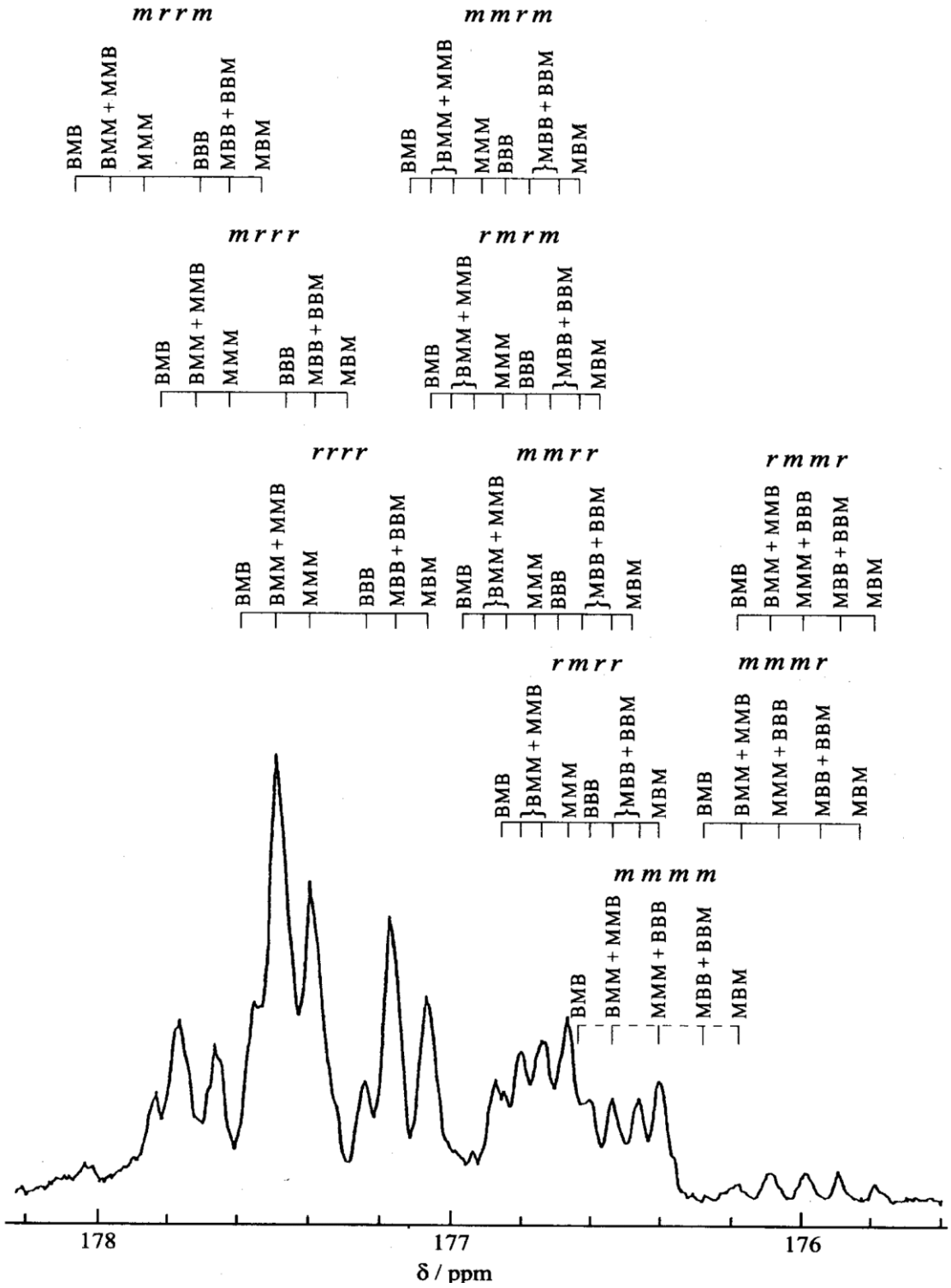


Figure 1.3. ^{13}C NMR spectra of the poly(methyl methacrylate-*co*-butyl methacrylate) (in $CDCl_3$ at 55℃,125MHz)

To extract quantitative information about microstructure of copolymers from those complicated resonances were not easily. Our most recent work deals that multivariate analysis of NMR spectra are good for structural analysis of copolymer and branched polymers [29-32]. For example, principal component analysis (PCA) of ^{13}C NMR spectra of methyl methacrylate (MMA) and *tert*-butyl methacrylate (TBMA), with different chemical compositions ratio, the homopolymers of the two methacrylates, and different blends of two methacrylates (MMA and TBMA) successfully extracted separately information of chemical composition and that of comonomer sequence [30].

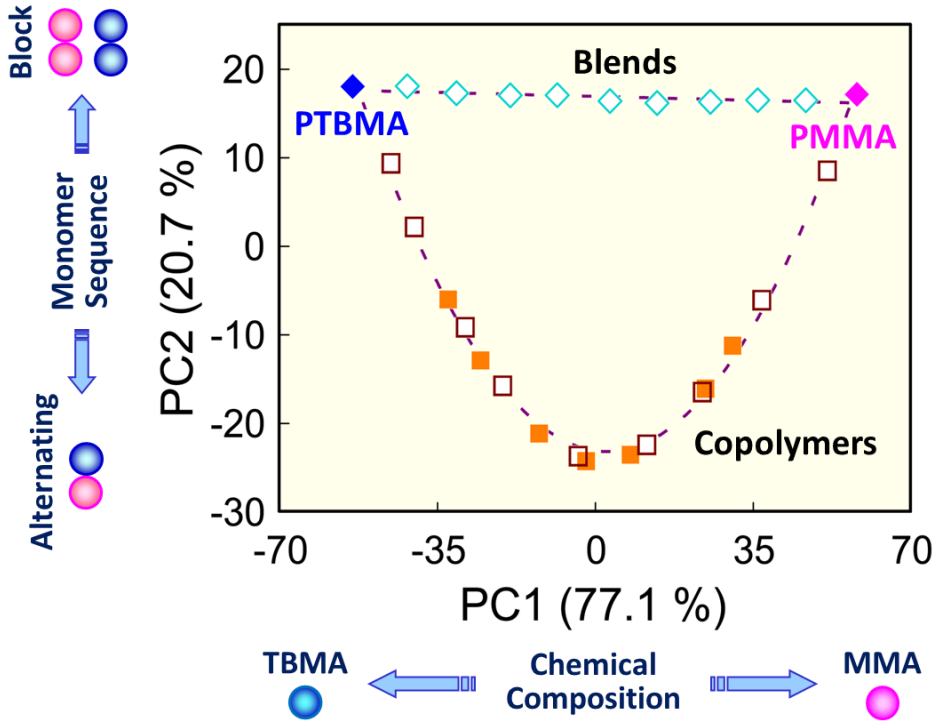


Figure 1.4. Principal Component Analysis of the MMA-TBMA System PC1-PC2 Score Plots.

1.2 Research Purpose

In the present work, we report the synthesis of a series of monomer sequences of methyl methacrylate-benzyl methacrylate (MMA-BnMA) copolymers through polymerization reactions of BnMA, including catalytic hydrogenolysis, acidic debenzylation, Saponification, and transesterification. Furthermore, we performed partial methylation after the benzylation of MAa as well as benzylation after methylation of MAa. The sequence of the individual monomers was analyzed through PCA to investigate comonomer sequence distribution in those copolymers for which these data could be obtained from ^{13}C NMR spectra. In other work, we prepared high stereoregularity PBnMA *via* anionic polymerization in order to assign the comonomer sequence. Prepare BnMA-MMA copolymer by partial saponification, partial acidic debenzylation, PBnMA and PMMA appropriate component with copolymer. Characterize the triad comonomer sequence of poly(BnMA-*co*-MMA) from carbonyl group by ^{13}C NMR spectroscopy. The findings of this work may facilitate the development of a new monomer sequence analysis.

Chapter 2 Review

2.1 Polymer Reactions

Methacrylates play a very important role because of the rich variety of monomers that can be prepared by modifying the ester group and the numerous practical applications of these polymers. For example, The cleavage of benzyl protecting groups of poly(benzyl acrylate) and poly(benzyl methacrylate) by catalytic hydrogenolysis under mild conditions[33]. The result of solubility test indicated the copolymer derived from catalytic hydrogenolysis that the sequence exhibited blocky. However, the monomer sequence did not further analyzed by spectroscopic. Poly(methacrylic acid-*co*-MMA) prepared by acidic debenzylation of PMMA with toluene sulfonic acid or Saponification of PMMA with NaOH solution [34]. But in this section only discuss reaction kinetics due to there are few literature examples of monomer sequence analysis of methacrylates copolymers prepared by polymer reaction [35-37].

2.2 Anionic Polymerization

The anionic polymerization of highly syndiotactic polymer required absolutely dehydrated environment, K. Hatada et al [38]. reported that PMMA obtained by adding t-C_4H_9Li as initiator and different catalyst species with various ratio, results of $(n\text{-}C_4H_9)_3Al$ and $(C_2H_5)_3Al$ demonstrated that *rr* triad was above 90%, showed as Table 2.1. On the other hand, add no catalyst will obtained high mm triad of PMMA. The tacticity can be controlled by tuning the ratio between *t*-C_4H_9Li and R_3Al.

Table 2.1. Polymerization of MMA with *t*-C_4H_9Li-R_3Al in toluene at −78 °C for 24 hr[a]

R	Al/Li	Yield (%)	Tacticity(%) mm	mr	rr	M_n[b] (Obsd)	M_n (Calcd)	M_w/M_n[c]
	0	93	78	16	6	10240[c]	4700	3.10
	1	93	57	26	17	6170[c]	4730	2.02
n-C_8H_{17}	1.5	19	37	19	44	3170[c]	1010	15.8
	3	89	0	7	92	4870	4520	1.13
	5[d]	75	0	4	96	4920	3830	1.18
n-C_4H_9	3	100	0	8	92	5510	5060	1.17
C_2H_5	3	99	0	10	90	5450	5020	1.18
CH_3	3	21	1	9	90	2920	1090	1.38
isoC_4H_9	3	70	60	26	14	5770	3540	1.77
	5	84	1	11	88	4620	4270	1.19

[a] MMA 10mmol, t-C_4H_9Li 0.20mmol, toluene 10ml.
[b] Determined by VPO. [c] Determined by GPC.
[d] Polymerization at -93°C.

T. Kawauchi et al.[24] reported two route to prepare highly stereoregularity polymethacrylates. One way carried out anionic polymerization of TMSMA with *t*-BuLi and $MeAl(ODBP)_2$ as initiator at −78 °C and obtained *st*-PMAa which has 96% rr triad, and then prepare copolymer via esterification with DBU, the scheme showed in Fig. 2.1. The other way was using *sec*-BuDPE-Li as initiator at −78°C synthesized *it*-poly(*t*-BuMA), then added HCl finally obtained *it*-PMAa which has 98% *mm* triad.

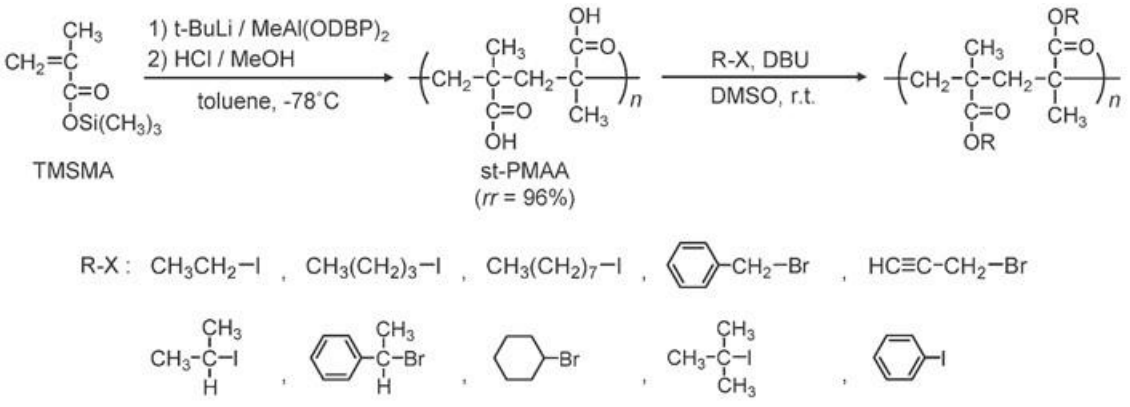


Figure 2.1. Synthetic Route of Highly Syndiotactic Polymethacrylates.

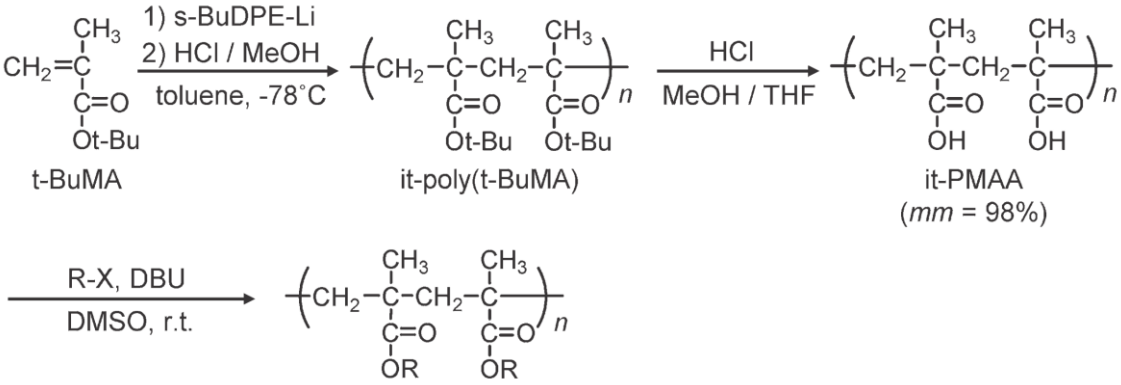


Figure 2.2. Synthetic Route of Highly isotactic Polymethacrylates.

T. Asakura et al.[39] reported a calculation method for the number-average sequence lengths of the triad and dyad sequences according to the following equations:

triad analysis

$$L_E = (F_{BEB} + F_{BEE} + F_{EEE})/(F_{BEB} + F_{BEE}/2) \quad (1)$$

$$L_B = (F_{EBE} + F_{BBE} + F_{BBB})/(F_{EBE} + F_{BBE}/2) \quad (2)$$

dyad analysis

$$L_E = (F_{EE} + F_{EB}/2)/(F_{EB}/2) \quad (3)$$

$$L_B = (F_{BB} + F_{EB}/2)/(F_{EB}/2) \quad (4)$$

Where Fi is molar fraction of the sequence. As shown in Fig. 2.3, the number-average sequence lengths, L_E and L_B, calculated from the triad sequences by ^{1}H NMR. The degree of randomness (R) means that the structural unit distribution and calculated with the following equation:

$$R = 1/L_E + 1/L_B$$

This study will synthesize high stereoregularity poly(benzyl methacrylate) (PBnMA) via anionic polymerization in order to assign the comonomer sequence. Prepare BnMA-MMA copolymer by saponification, PBnMA and PMMA appropriate component with copolymer. Characterize the triad comonomer sequence of poly(BnMA-co-MMA) from

carbonyl group by ^{13}C NMR spectroscopy.

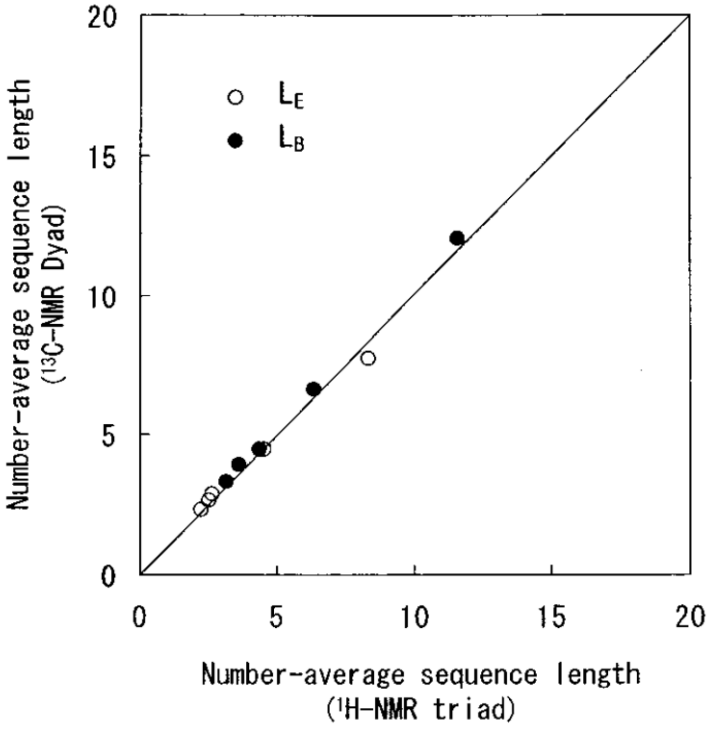


Figure 2.3. Comparison of the number-average sequence lengths of PET units (L_E) and PBT units (L_B) calculated from the triad sequences obtained from $_1H$ NMR and dyad sequences obtained from ^{13}C NMR for several poly(ethylene/butylene terephthalate) copolymers with different sequences of the comonomer.

2.3 Materials

1. Benzyl methacrylate (BnMA, 98%) was purchased from Mitsubishi rayon and distilled immediately prior to use.
2. *tert*-Butyllithium (*t*-BuLi) was purchased from TCI and used as pentane solution.
3. Triethylaluminium (Et_3Al) was purchased from TCI and used as toluene solution.
4. Trifluoroaceticacid, TFA, $C_2HF_3O_2$, reagent grade, TCI.
5. Potassium hydroxide (KOH), reagent grade, Kishida Chemical.
6. 15-crown-ether, ($C_{10}H_{20}O_5$, 15C5), industry grade, Kanto Chemical Industry.

7. 18-crown-ether, ($C_{12}H_{24}O_6$, 18C6), industry grade, Kanto Chemical Industry.
8. Tetrabutylammonium Hydroxide (TBAH) (37% in methanol), $C_{16}H_{37}NO$, TCI.
9. 1, 8-diazabicyclo[5,4,0]undec-7-ene (DBU), $C_9H_{16}N_2$,TCI.
10. Benzyl Bromide, TCI.
11. 2-Fluorobenzoate, C_6H_4BrF, TCI.
12. Methoxymethane, CH_3OCH_3, TCI.
13. N-methyl-*n*-hitroso-*p*-toluenselfonamide, $C_8H_{10}N_2O_3S$, reagent grade, TCI。
14. 2-(2-Ethoxyethoxy)ethanol, $C_6H_{14}O_3$, reagent grade, TCI.
15. *tert*-Butyl methyl ether, $CH_3OC(CH_3)_3$, reagent grade, TCI.
16. Tertahydrofuran (THF), C_4H_8O, Kishida Chemical.
17. *n*-Hexane, C_6H_{14}, Kishida Chemical.
18. Toluene, C_7H_8, Kishida Chemical.
19. Methanol, CH_3OH, monomers of industrial grade.
20. Dimethyl Solfoxide-d_6, C_2H_6SO Kanto Chemical Industry
21. Deuterated Chloroform-*d*, $CDCl_3$, Merck.
22. Deuterated Benzene-d_6, C_6D_6, TCI.
23. Deuterated Dimethyl Solfoxide-d_6, C_2D_6SO, Wako.
24. Tetramethylsilane (TMS), $C_4H_{12}Si$, TCI

2.4 Measurements

1. Rotaryevaporator.
2. Nuclear Magnetic Resonance, JEOL, JNM-ECA500WB , JNM-ECX400P。
3. JEOL Alice2 ver.5 for metabolome ver.1.6 software.
4. Pattern Recognition System Sirius ver. 7.0 software.
5. Size-exclusion chromatography (SEC).

2.5 Synthesis of Polymers

2.5.1 Synthesis of poly(benzyl methacrylate) *via* Radical Polymerization

Polymerization was carried out in a three-necked 300-mL round-bottom flask equipped with a magnetic stirrer and nitrogen supply. To a 20 wt% solution of BnMA in toluene, AIBN (0.5 mol% of the monomer) was added, and the solution was stirred at 60 °C for 24 h. The polymer was recovered by precipitation in an excess amount of methanol, and dried under vacuum for 24 h. Copolymers of MMA and BnMA with various compositions were prepared in a similar manner. Table 2.1 summarizes the chemical composition (mol% in MMA units) and molecular weight of the polymer samples used in the present work. The nine copolymers and two homopolymers were abbreviated as C-14 to C-93 and H0 to H100, respectively, in which the number corresponds to the percentage of MMA units. Table 2.2 lists the chemical compositions of the blends of the PMMA (H100) and PBnMA (H0) as determined by ^{1}H NMR.

Table 2.2. Homopolymers and copolymers of MMA and BnMA prepared by radical polymerization in toluene at 60 °C[a]

Sample code	MMA (mol%)		Yield (%)	M_n[c] / 10^4	M_w/M_n[c]
	Feed[a]	Copolymer[b]			
H0[d]	0	0	94.0	5.1	2.6
C14	9.9	14.1	89.1	6.9	1.8
C27	20.0	26.6	87.9	7.1	1.7
C39	30.0	38.5	87.7	5.6	2.8
C49	39.8	48.7	86.8	5.6	1.8
C59	48.9	59.4	88.0	5.3	2.7
C69	60.1	68.6	84.7	5.7	1.7
C77	70.0	77.2	81.1	5.8	2.3
C84	79.7	83.9	79.2	5.5	1.6
C93	90.0	92.9	85.3	4.9	1.5
H100[e]	100	100	81.8	5.3	1.4

[a] AIBN was used as the initiator (0.5 mol% of monomer).

[b] Determined by ^{1}H NMR in $CDCl_3$ at 55 °C.

[c] Determined by SEC calibrated against standard PMMA samples.

[d] Stereoregularity in triads, *rr* : *rm* : *mm* = 60.0 : 35.6 : 4.4.

[e] Stereoregularity in triads, *rr* : *rm* : *mm* = 62.0 : 33.8 : 4.2.

Table 2.3. MMA unit compositions of the blends of PMMA (H100) and PBnMA (H0)

Sample code	MMA (mol %)[a]
B12	11.8
B20	19.3
B30	29.7
B39	38.8
B49	48.5
B59	58.2
B69	68.7
B78	77.7
B86	86.1

[a] Determined by ^{1}H NMR in $CDCl_3$ at 55 °C.

2.5.2 Synthesis of Highly Isotactic poly(benzyl methacrylate)

Anionic polymerization of BnMA was carried out a dry glass ampule under a dry argon atmosphere. The initiator solution was prepared by adding *t*-BuLi (2 mL) in toluene (100 mL) at -60 °C. The polymerization reaction was initiated by adding BnMA (20 mL) to the initiator solution at -60 °C. After 48 h, the reaction was quenched with methanol containing a small amount of aqueous 12N HCl. The polymer was poured into a large amount of n-hexane, and the precipitate was collected by filtration, and then dried under vacuum for 24h.

2.5.3 Synthesis of Highly Syndiotactic poly(benzyl methacrylate)

Syndiotactic-specific anionic polymerization of BnMA using a combination of *t*-BuLi and Et_3Al as initiator was carried out a dry glass ampule under a dry argon atmosphere. The initiator solution was prepared by adding *t*-BuLi (0.67 mL) to a Et_3Al

(3.2 mL) solution in toluene (100 mL) at -78 °C and keeping for 10 min at -78 °C. The polymerization reaction was initiated by adding BnMA (20 mL) slowly to the initiator solution at -78 °C. After completion of the polymerization, the reaction was quenched with methanol containing a small amount of aqueous 12 N HCl. The polymer was poured into a large amount of n-hexane, and the precipitate was collected by filtration, washed with acetone several times, and then dried under vacuum for 24h.

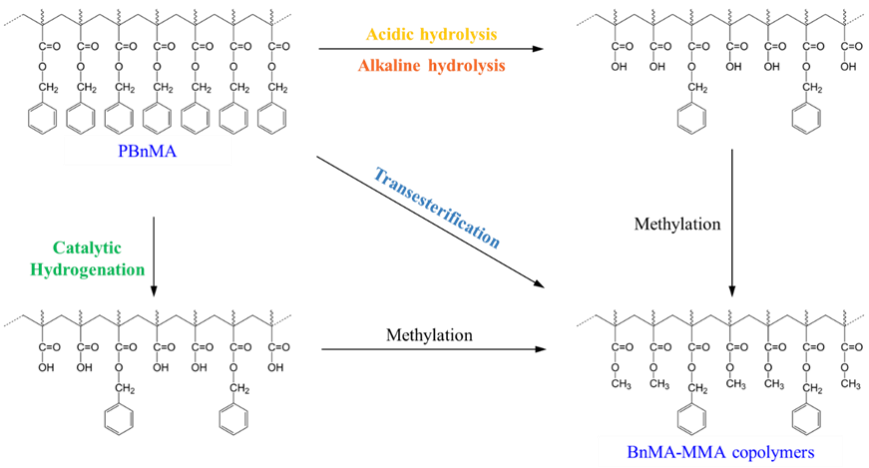
2.5.4 Synthesis of poly(methacrylic acid) *via* Acidic Debenzylation

The PBnMA(28 mmol) was dissolved in 150 mL TFA in a one-necked 300 mL round-bottomed flask equipped with magnetic stirrer in reflux and an oil bath at 70 °C for 4h. The reaction was terminated of TFA removal by purification and the polymeric product recovered was by addition to an excess n-hexane.

2.6 Polymer Reaction of PbnMA

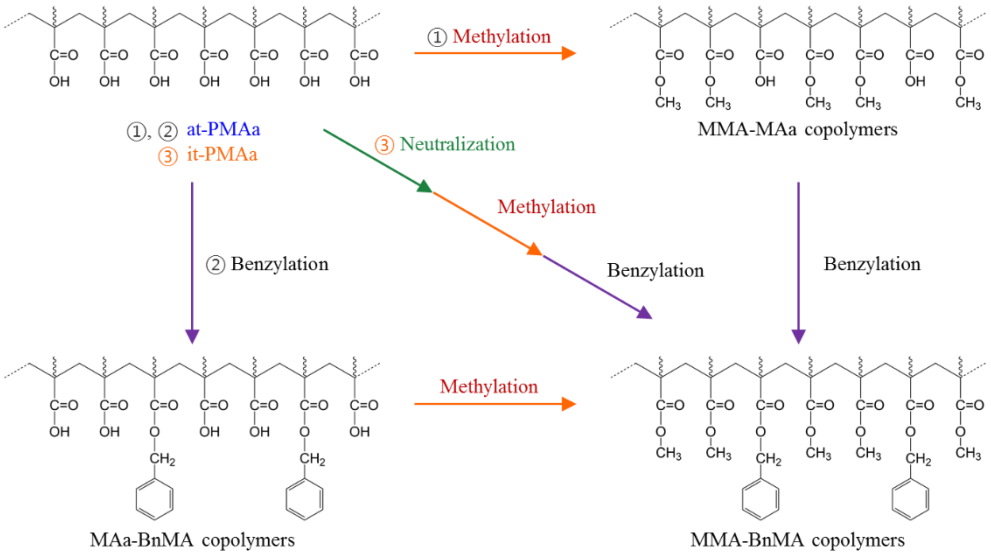
The PBnMA which can be cleaved either via catalytic hydrogenolysis, acidic debenzylation, saponification and transesterification. Copolymers of PBnMA and methacrylic acid (MAa) were converted to BnMA-MMA copolymers by methylation with diazomethane prior to the analysis. (Scheme 2.1)

Scheme 2.1. Polymer reactions of *at*-, *it*-, *st*-PBnMA



Partial neutralization of PMAa followed by methylation to MMA-MAa copolymer. Copolymer of MMA-MAa were converted to MMA-BnMA copolymers by benzylation prior to the analysis. Furthermore, partial methylation of PMAa followed by benzylation to MMA-BnMA copolymer. Benzylation of PMAa followed by methylation with diazomethane. (Scheme 2.2)

Scheme 2.2. Polymer reactions of *at*-poly(MAa) and *it*-poly(MAa)



2.6.1 Catalytic Hydrogenolysis (CH) of the *at*-PbnMA

Partial debenzylation of the PBnMA was achieved through catalytic hydrogenolysis. Accordingly, PBnMA (H0,0.5g corresponding to 2.8 mmol in BnMA units) was dissolved in 30 mL of a mixture of THF and methanol (5:1 v/v, 30 mL) in a one-necked 100-mL round-bottom flask fitted with a tap and balloon. To this solution, 0.25 g of Pd/C (5%) catalyst was added, with stirring, under a hydrogen atmosphere (1 atm) at ambient temperature. After complete hydrogenation, the solution was filtered to remove solid catalyst residues, and the polymer was recovered through precipitation with excess n-hexane. The resultant copolymers of BnMA and MAa were converted to MMA–BnMA

copolymers through methylation with diazomethane. After 24 h, the precipitated polymer was collected through filtration and dried overnight in vacuum at room temperature. The copolymers were precipitated with excess methanol, recovered through filtration, and dried under vacuum at ambient temperature for 24 h. Completed chemical conversion was confirmed by ^{1}H NMR spectroscopy. Table 2.4 lists the experimental conditions required to obtain the polymer products CH18–CH65 and their chemical compositions (mol% in MMA units).

2.6.2 Acidic Debenzylation (AD) of the PbnMA

PBnMA (H0, 0.5 g) was dissolved in 15 mL of TFA in a one-necked 100-mL round-bottom flask fitted with a cap. Next, the solution was evaporated using a rotary evaporator, and the copolymers were recovered by adding excess n-hexane. Copolymers of PBnMA and MAa were converted to poly(MMA–BnMA)s through methylation with diazomethane. Complete chemical conversion was confirmed by ^{1}H NMR spectroscopy. The experimental conditions required to obtain the copolymer products AD12–AD91 are shown in Table 2.5.

2.6.3 Saponification (SP) of the PbnMA

PBnMA (H0, 0.5 g) was dissolved in 15 mL of a mixture of toluene or dioxane containing a 15-fold excess of KOH or$HOCH_3$ (42 mmol, solution in 2 mL of wather) and 18-crown-6 (0.7 mmol) in a one-necked 100-mL round-bottom flask fitted with a condenser. After the reaction, HCl was added to the solution, and the solution for neutralization and the mixture was stirred overnight at room temperature. Subsequently, THF was added to the solution to remove KCl before filtration. The excess THF was removed using a rotary evaporator and the copolymers were precipitated using excess n-

hexane. Poly(MAa-BnMA)s were converted to poly(MMA-BnMA)s through methylation with diazomethane. Complete chemical conversion was confirmed by ^{1}H NMR spectroscopy. The experimental conditions required to obtain the copolymer products SP50-SP63 are shown in Table 2.6.

2.6.4 Transesterification (TE) of the *at*-PbnMA

PBnMA (H0, 0.5 g) was dissolved in 16 mL of a mixture of dioxane containing 8mL of methanol and $KOCH_3$ (42 mmol) solution in a one-necked 100-mL round-bottom flask fitted with a condenser. After the reaction at 85°C, aqueous HCl was added to the solution, and the solution was stirred overnight at room temperature. Subsequently, THF was added to the solution to remove KCl by filtration. Excess THF was removed using a rotary evaporator and the copolymers were precipitated to excess n-hexane. The experimental conditions required to obtain the copolymer products TE23-92 are shown in Table 2.7). The absence of MAa units in the TE copolymers was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

2.6.5 Two-Step Benzylation–Methylation (BM) of the poly(MAa)

PMAa was prepared by full debenzylation of PBnMA (H0) with TFA in the manner described above (AD, 80 °C, 24 h). In a one-necked 100-mL round-bottom flask, 0.4 g of PMAa (4.64 mmol in MAa units) was dissolved in 20 mL of DMSO. To the solution, 0.397g of benzyl bromide (2.32 mmol) and 0.354 g of DBU (2.32 mmol) was added, and the mixture was allowed to stand overnight at room temperature. The copolymer was recovered by precipitation in excess water. The resultant copolymer of MAa and BnMA was converted to MMA–BnMA copolymer through methylation with diazomethane.

The chemical composition of the copolymer was 57.0 % in MMA units, and thus the sample code BM57 was given to this copolymer (Table 2.8).

2.6.6 Methylzation–Benzylation of the poly(MAa) Unit

In a one-necked 100-mL round-bottom flask, 0.4 g of PMAa was dissolved in 20 mL of a mixture of DMSO and methanol (8:2 v/v). A diazomethane solution (0.5 eq) was added to the polymer solution, and the mixture was stirred overnight at room temperature. The solvent was removed from the reaction mixture by evaporation, and the resultant copolymer of MMA and MAa was recovered by precipitation in excess *n*-hexane. The MMA-MAa copolymer was converted to MMA-BnMA copolymer (MB49 in Table 2.9) by a procedure similar to that described above (BM).

2.7 Multivariate Analysis of ^{13}C NMR Spectra

^{1}H and ^{13}C NMR spectra of the samples were measured in chloroform-*d* (8% w/v) at 55°C by using a JEOL ECX400 spectrometer equipped with a 10-mm multinuclear probe (^{1}H: 45° pulse (8.5 μs), pulse repetition = 8.90 s, 16 scans, ^{13}C: 45° pulse (7.5 μs), pulse repetition = 2.73 s, 5000 scans, with ^{1}H broadband decoupling). A line-broadening factor of 2.0 Hz was applied before Fourier transformation of the ^{13}C NMR data. The chemical composition was determined from the relative intensities of ^{1}H NMR signals caused by the ester groups of the MMA and BnMA units. Tetramethylsilane and the residual chloroform in $CDCl_3$ were used as an internal reference at 0.00 ppm and 7.27 ppm in ^{1}H NMR and at 0.00 ppm and 77.0 ppm in ^{13}C NMR.

Bucket integration was performed for the spectral regions 15–23 ppm (the α-methyl groups) and 175–179 ppm (the carbonyl groups) at an interval of 0.01 ppm. The sum of

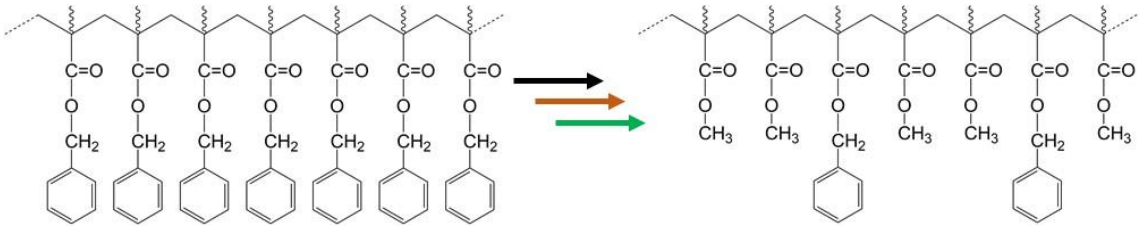
the integral intensities in each spectral region was normalized to 100. The average integral intensity was subtracted from each integral intensity. Each dataset thus obtained comprised 32 mean-centered bucket integral values. The bucket integration and PCA of the datasets were carried out using Alice2 ver.5 for metabolome ver.1.6 software (JEOL Ltd., Tokyo, Japan).

2.8 Size–Exclusion Chromatography (SEC) Measurement

SEC was performed using an HLC8220 chromatograph (Tosoh, Yamaguchi, Japan) equipped with TSK gel columns (SuperHM-M (6.5 mm ID×150 mm) and SuperHM-H (6.5 mm ID×150 mm), Tosoh). THF was used as the eluent, at 40 °C and a flow rate of 0.35 ml min^{-1}. The evaporative light scattering detector (ELSD) signal was measured using a Polymer Laboratories PL-ELS-2100 detector. The calibration curve was based on nine narrow molecular weight (1860, 4950, 10 570, 30 620, 67 400, 121 600, 332 800, and 679 000 g mol^{-1}) linear PMMA standards also supplied by Polymer Laboratories.

Chapter 3 Multivariate Analysis of Composition and Monomer Sequence of Atactic poly(MMA-*co*-BnMA)s Prepared by Various Polymer Reactions

Various monomer sequences of poly(MAa-*co*-BnMA)s were prepared by various polymer reactions from atactic PBnMA. After the poly(MAa-*co*-BnMA)s converted to copolymers of poly(MMA-*co*-BnMA)s by methylation with diazomethane. On the other hand, PBnMA were completely converted PMAa *via* acidic debenzylation. Poly(MMA-BnMA)s were prepared by methylation and then benzylation or inverse way of benzylation-methylation of PMAa. The characterization of monomer sequence by ^{13}C NMR were too complex to analyze clearly. Hence, the monomer sequence of poly(MMA-*co*-BnMA)s were determined by multivariate analysis.



3.1 Principal Component Score Plots for the ^{13}C NMR Spectra of Radical Copolymers and Homopolymer Blends: Constructing the Reference Framework for Monomer Sequence Analysis

Figure 3.1 shows the ^{13}C NMR spectra of the polymer products obtained by polymerizations. Table 3.1 shows summarizes the functional groups and chemical shift detail of PMMA, PBnMA, radical copolymer, and homopolymer blend. The ^{13}C NMR spectra of the original MMA and BnMA homopolymer, radical copolymer, and homopolymer blend is also presented in Figure 3.1. PMMA and PBnMA having same functional group of α-methyl (1), methylene (4), backbone quaternary carbon (2), and carbonyl group (8), respective. The functional groups of ^{13}C NMR spectra of copolymers often show overlapped splitting due to monomer sequence and configurational sequence. In other hand, the benzyl group side chain (6, 7) of PBnMA show the complicated spectra in ^{13}C NMR (Figure 3.1). We selected three functional group region of α-methyl, backbone quaternary carbon, carbonyl responded (co)polymers in order to further analysis.

Table 3.1. Function groups and chemical shift of PMMA and PBnMA.

Number	Functional group	Chemical shift region (ppm)
1	α-methyl	14.5 – 22.0
2	Backbone quaternary carbon	43.5 – 46.5
3	Methyl group side chain of PMMA	44.2 – 58.2
4	Methylene region	44.2 – 58.2
5	Methylene group side chain of PBnMA	66.0 – 68.0
6	Benzyl group of PBnMA	127.5 – 129.0
7	Benzyl group of PBnMA	135.0 – 136.5
8	Carbonyl region	175.0 – 179.0

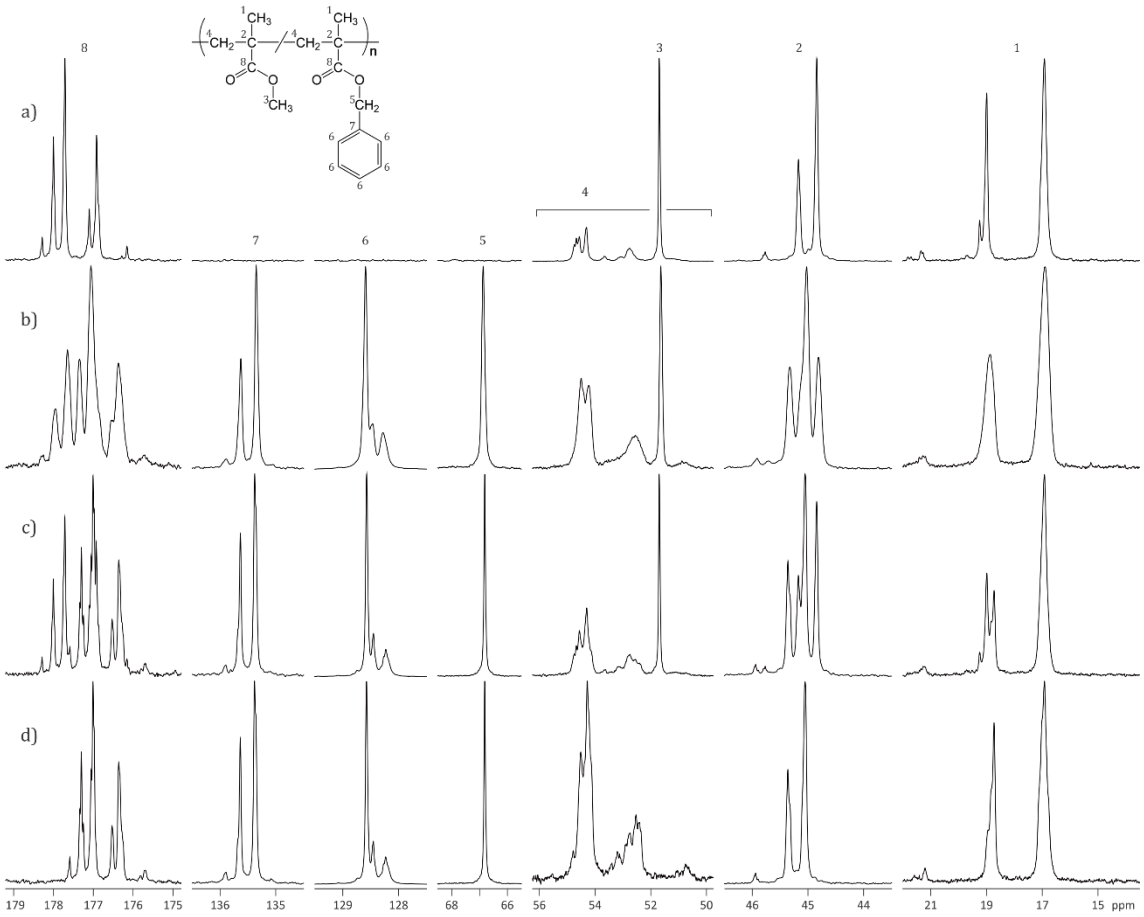


Figure 3.1. ^{13}C NMR spectra in chloroform-*d* of (a) PMMA [H0], (b) radical copolymer [C49], (c) homopolymer blend and (d) PBnMA [H100].

In the ^{13}C NMR spectra of MMA-BnMA copolymers, the influence of monomer sequences and configurational sequences appeared mostly in the resonances due to the α-methyl groups and carbonyl groups. Figure 3.2 illustrates the resonance patterns for the homopolymers (H0 and H100), a blend of the homopolymers (B49), and a radical copolymer (C49). The resonance patterns for the homopolymers are typical of those for polymethacrylates obtained by free-radical polymerization, which reflects the configurational triads (α-methyl groups) or pentads (carbonyl groups) in atactic (or syndiotactic-rich) polymer chains. The triad tacticities (*rr* : *rm* : *mm*) determined from the α-methyl resonances were 60.0 : 35.6 : 4.4 for H0 and 62.0 : 33.8 : 4.2 for H100. It is

clear that the resonances for the copolymer are broader than those for the homopolymer blend with a similar chemical composition. The broadness of the resonances arises from the MMA-BnMA cross-linkages which do not exist in the homopolymer blend. However, further information about the monomer sequences is directly unavailable from the broad resonances.

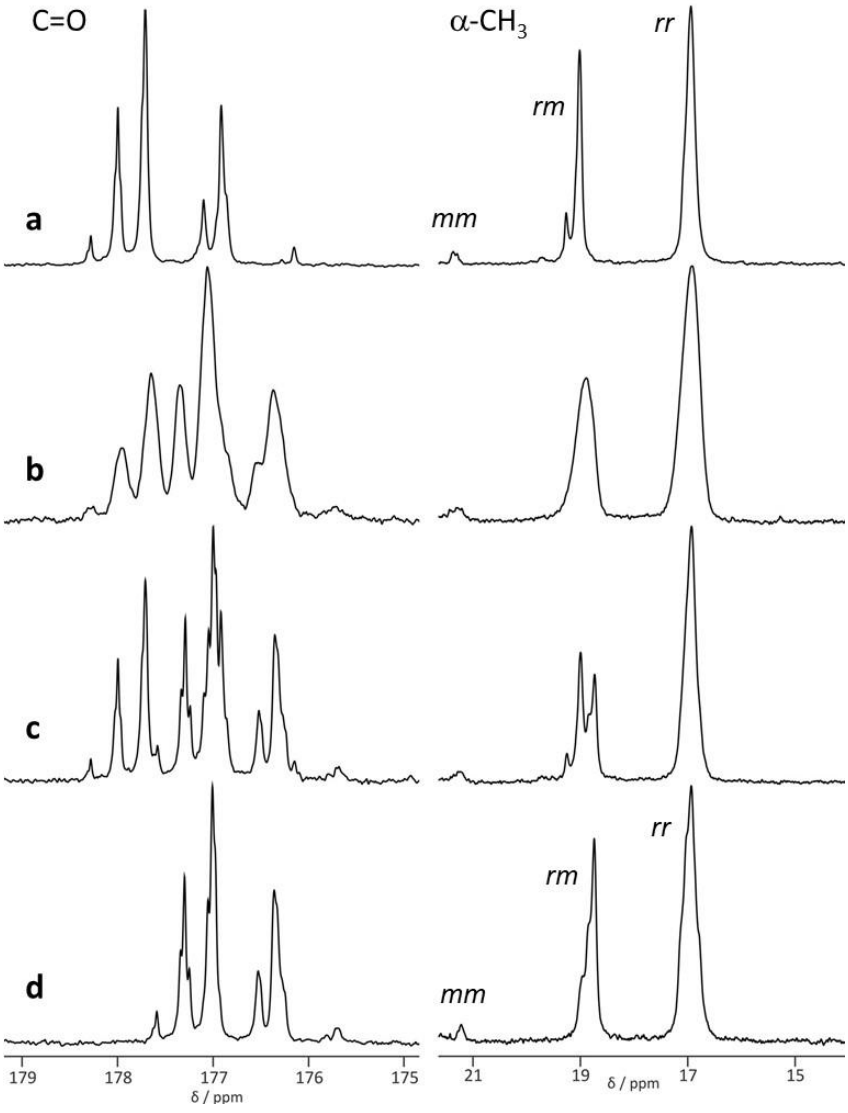


Figure 3.2. ^{13}C NMR spectra due to the carbonyl and α-methyl of (a) PMMA [H100], (b) radical copolymer [C49], (c) homopolymer blend [B49] and (d) PBnMA [H0] in chloroform-*d* at 55℃ and 100 MHz.

To extract useful information about the monomer sequences from the resonances, PCA was carried out for the dataset comprising the α-methyl and carbonyl resonances of the two homopolymers, nine radical copolymers with various compositions (C14 to C93 in Table 3.2), and nine blends of homopolymers with various blend ratios (B12 to B86 in Table 3.3). Figure 3.3 shows the principal component score plots produced by the analysis. Contribution rates for the first and second principal components (PC1 and PC2) were 84.8 % and 12.6 %, respectively, indicating that the spectral information of the dataset was explained well by these two parameters (a cumulative contribution rate of 97.4 %). The plots of the homopolymers (● ●) and homopolymer blends(■) represented a linear relationship with PC1, while the plots of the copolymers (◆) exhibited a parabolic relationship between PC1 and PC2. PC1 scores were proportional to the MMA composition of the samples. PC2 showed a minimum at around the plot of copolymer C49, which has a nearly equimolar composition of MMA and BnMA. Therefore, PC2 is reasonably assumed to correlate to the abundance of MMA-BnMA cross-linkages. The product of comonomer reactivity ratios $r_1 \times r_2$ for the free-radical copolymerization of MMA and BnMA in the literature (0.90–1.08)[40] suggest that the copolymers C14 to C93 are statistical copolymers with ideally random sequences. The principal component score plots for the datasets are thus suitable as a reference framework for the sequence analysis described below. We obtained the PCA score plots for monomers synthesized through catalytic hydrogenolysis, acidic debenzylation, Saponification, and transesterification of the PMMA-BnMA copolymers or poly(MMA-BnMA)s obtained using PMAa through methylation after benzylation of MAa or through benzylation after methylation for sequence analysis .

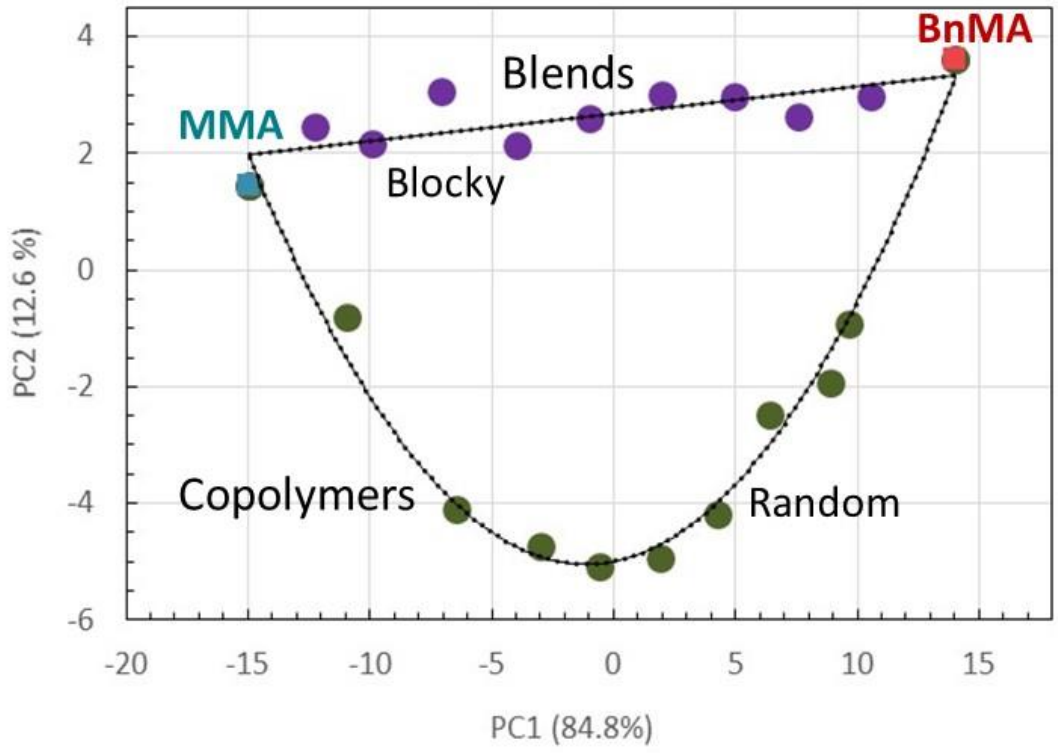


Figure 3.3. Principal component score plots for the carbonyl and α-methyl ^{13}C NMR signals of homopolymers (●●), homopolymer blends (■) and radical copolymers (◆). See Figure 3.3 for the abbreviations a – d.

3.2 Principal Component Analysis of Monomer Sequence in the MMA-BnMA Copolymers Prepared by Various Polymer Reactions

Scheme 3.1 shows the various routes followed the selective deprotection of BnMA. Four routes of poly(MMA-BnMA)s with either partial catalytic hydrogenolysis, acidic debenzylation, saponification and transesterification were obtained, while Table 3.4. The BnMA could also be converted to MAa units with either partial catalytic hydrogenolysis, acidic debenzylation, saponification and transesterification. The poly(MAa-BnMA)s were converted to poly(MMA-BnMA)s by methylation. The product obtained after each of the above processing steps were characterized using ^{1}H, ^{13}C NMR spectroscopy, and principal component analysis (PCA), and the results are presented in the following sections.

Scheme 3.1. Cleavage sequences followed for the selective deprotection of the BnMA that all the way to prepare poly(MMA-*co*-BnMA)s[a]

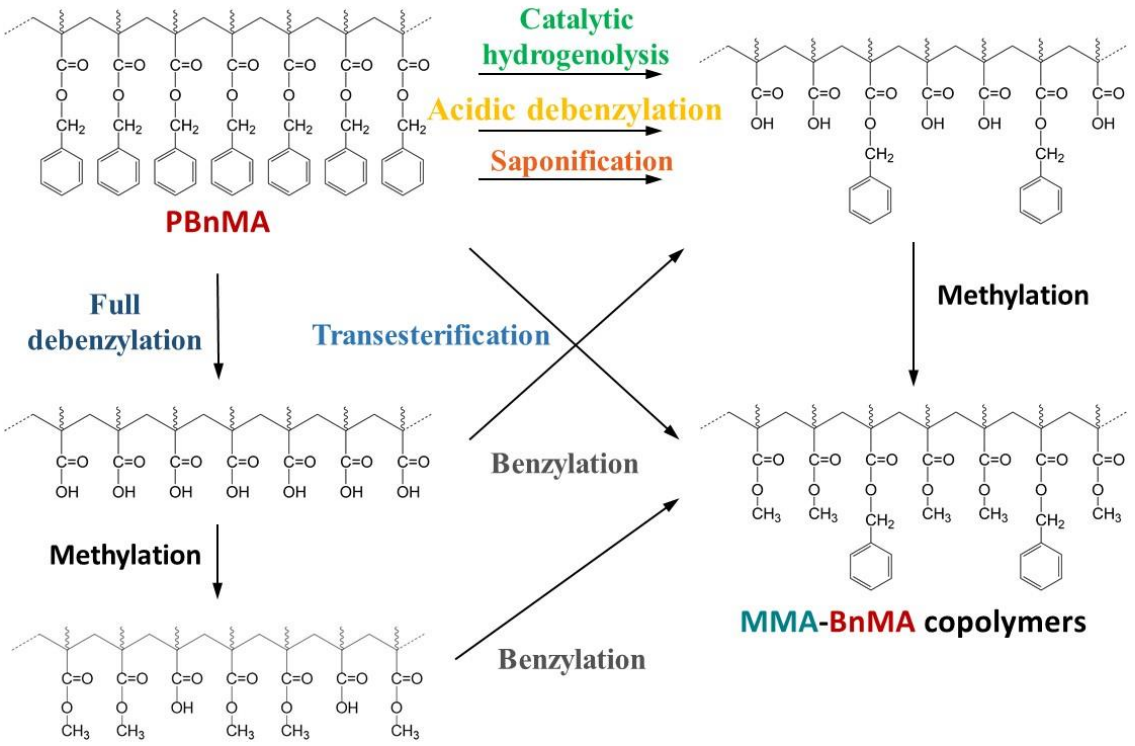


Table 3.4. Reaction conditions for the preparation of MMA-BnMA copolymers by partial modification of PBnMA through catalytic hydrogenation (CH), acidic debenzylation (AD), saponification (SP), and transesterification (TE), and by two-step esterification of PMAa (BM and MB)

Sample code	MMA (mol%)[a]	Reactant	Catalyst	Solvent	Temp. (°C)	Time (h)
CH18	18.0	H_2	Pd/C	THF/MeOH	r.t.	1
CH44	44.0	H_2	Pd/C	THF/MeOH	r.t.	3
CH50	50.0	H_2	Pd/C	THF/MeOH	r.t.	4
CH65	65.0	H_2	Pd/C	THF/MeOH	r.t.	5
AD12	12.0	TFA	-	-	50	1
AD32	32.0	TFA	-	-	50	2
AD34	33.7	TFA	-	-	50	3
AD41	41.0	TFA	-	-	50	4
AD52	52.0	TFA	-	-	50	6
AD64	64.0	TFA	-	-	60	4
AD91	91.0	TFA	-	-	70	8
SP50	50.2	H_2O/KOH	18-crown-6	Toluene	100	48
SP59	59.0	H_2O/$KOCH_3$	18-crown-6	Toluene	85	48
SP63	62.4	H_2O/$KOCH_3$	18-crown-6	Dioxane	85	48
TE23	22.9	MeOH	$KOCH_3$	Dioxane	85	12
TE33	33.2	MeOH	$KOCH_3$	Dioxane	85	24
TE49	48.8	MeOH	$KOCH_3$	Dioxane	85	36
TE85	85.4	MeOH	$KOCH_3$	Dioxane	85	48
TE92	92.0	MeOH	$KOCH_3$	Dioxane	85	60
BM57	57.0	Benzyl bromide	DBU	DMSO	r.t.	24
MB49	49.3	CH_2N_2	-	DMSO/MeOH	r.t.	24

[a] Determined by ^1H NMR in $CDCl_3$ at 55 °C.

3.2.1 Characterization of poly(MMA-BnMA)s Obtained by PBnMA from Various Polymer Reactions

Scheme 1 depicts the different routes for the selective partial deprotection of PBnMA. The four routes for synthesis of poly(MMA-BnMA)s were partial catalytic hydrogenolysis, acidic debenzylation, Saponification, and transesterification. Table 3.5 summarizes the results. The benzyl ester groups can be selectively cleaved under relatively mild conditions through catalytic hydrogenolysis [33, 34]. Such selectivity has been utilized recently in synthesis polymer chemistry. PBnMA can be converted to PMAa through catalytic hydrogenolysis using a palladium catalyst. The poly(MAa-BnMA)s were converted to copolymers of poly(MMA-BnMA)s through methylation with diazomethane. Figure 3.7 illustrates the ^{13}C NMR spectra of the carbonyl region of the polymer products obtained by subjecting PBnMA to catalytic hydrogenolysis (a), acidic debenzylation (b), Saponification (c), or transesterification (d). The poly(MMA-BnMA)s have similar chemical compositions (50.0%, 52.0%, 50.2%, and 48.8% in MMA units, respectively). The copolymers derived from catalytic hydrogenolysis were analogous to the homopolymer blends in Figure 3.7.

Moreover, the PBnMA fragment underwent deprotection after the addition of TFA, KOH, or $KOCH_3$ with 18-crown-6. Hence, the MAa units were converted to MMA units, leading to the formation of poly(MMA-BnMA)s. The results for the copolymers and those for poly(MMA-BnMA)s obtained by subjecting PBnMA to acidic debenzylation with methylation were similar. We estimated that the monomer sequence of the copolymers derived from acidic debenzylation was nearly random in Figure 3.4b.

Alternatively, polymeric products that were obtained through Saponification were similar to the copolymers synthesized through acidic debenzylation, and chemical shifts

were observed at 177.4, 177.7, and 178.0 ppm in the ^{13}C NMR spectrum in Figure 3.5c

The ^{13}C NMR spectrum indicating that the monomer sequence of poly(MMA-BnMA)s synthesized through Saponification with diazomethane is slightly random. We estimated that the copolymers derived from Saponification were partially composed of alternating monomers.

Copolymers of poly(MMA-BnMA)s were prepared through the transesterification of PBnMA. PBnMA can be converted to poly(MMA-BnMA) through transesterification instead of methylation. Comparing the spectra in Figure 3.6 b, c, and d illustrates that transesterification of PBnMA generated a similar spectrum to that of the copolymers synthesized through acidic and Saponification by using PBnMA. We estimated that the monomer sequence in the copolymers derived from transesterification was partially random and alternating.

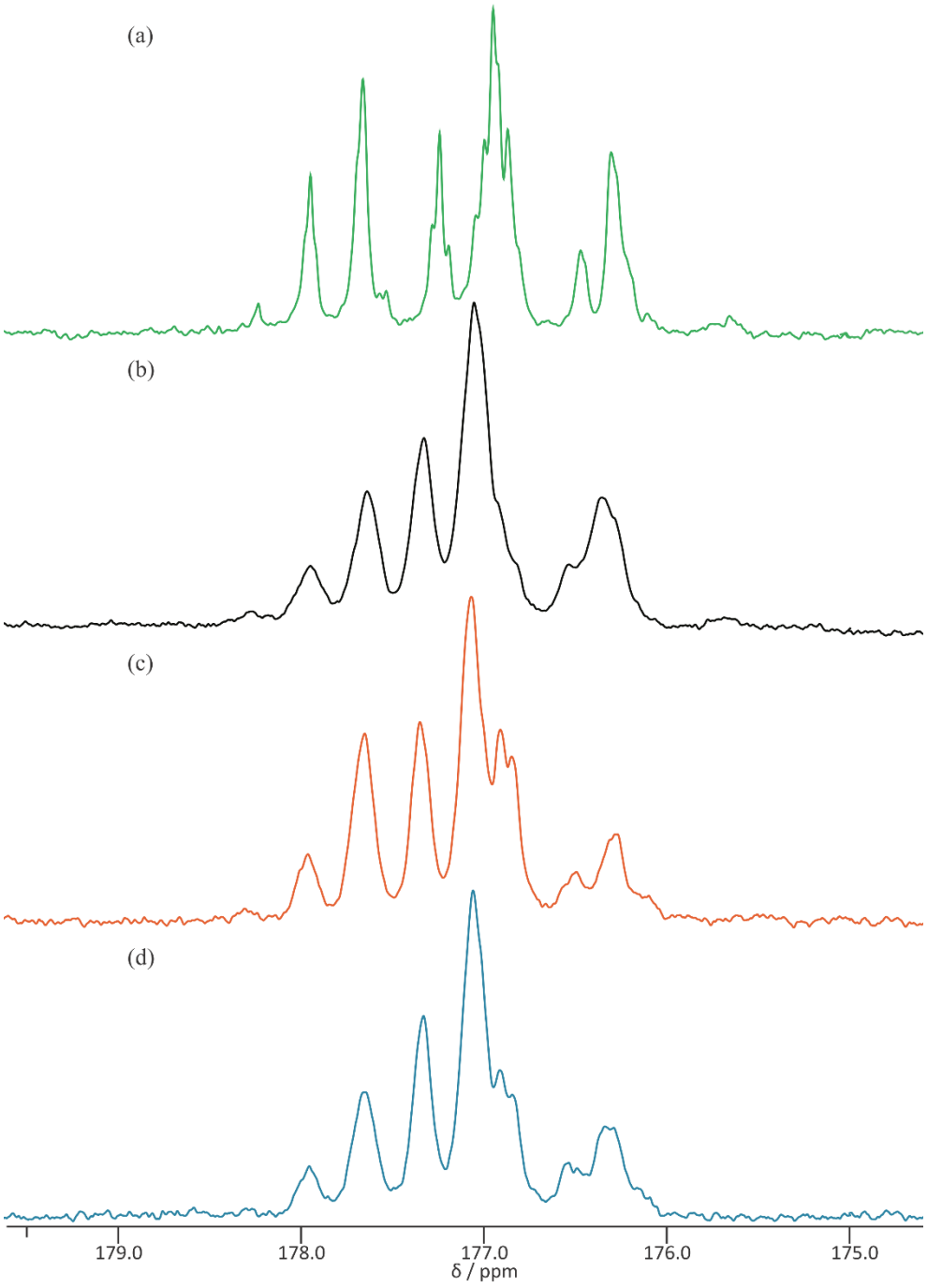


Figure 3.7. ^{13}C NMR spectra due to the carbonyl carbon of poly(MMA-BnMA)s obtained by PBnMA to catalytic hydrogenolysis (a), acidic debenzylation (b), saponification (c), and transesterification (d)

3.2.2 Poly(methacrylic acid) followed by Methylation-Benzylation or Benzylation-Methylation to MMA-BnMA Copolymer

PBnMA can be completely converted to PMAa through acidic debenzylation using TFA. PMAa can be converted to poly(MAa-BnMA)s through benzylation. After the reaction, the poly(MAa-BnMA)s were converted to copolymers of poly(MMA-BnMA)s through methylation with diazomethane [BM57]. By contrast, PMAa can be recovered through methylation. Subsequently, the polymer products were converted to copolymers of poly(MMA-BnMA)s through benzylation [MB49]. The ^{13}C NMR spectra of the carbonyl carbon of a homopolymer blend, the polymer products prepared from PMAa through benzylation–methylation, the products prepared through methylation–benzylation, and a copolymer prepared through copolymerization are shown in Figure 3.10 a, b, c, and d, respectively. The spectra of the poly(MMA-BnMA)s that were synthesized through benzylation–methylation and methylation–benzylation were similar to that of the copolymer. The monomer sequence of the copolymers derived from methylation–benzylation was somewhat random. Moreover, at 177.1 ppm, the poly(MMA-BnMA)s have a single peak in Figure 3.8c but multiple peaks in Figure 3.9b.

We forecast the monomer sequence in the copolymer derived from methylation-benzylation that were somewhat random, and the copolymer derived from benzylation-methylation need to further analysis.

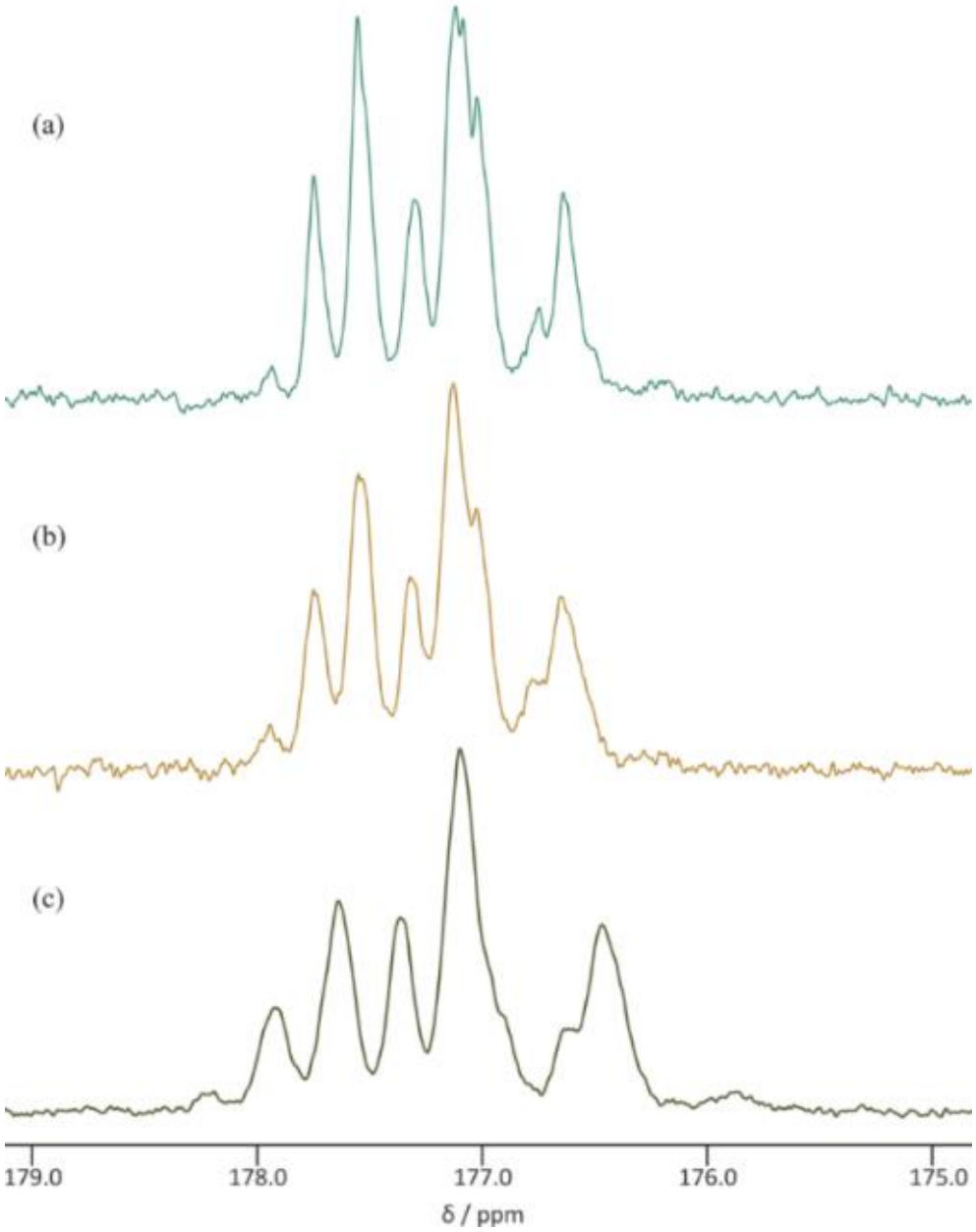


Figure 3.10. ^{13}C NMR spectra due to the carbonyl group of region between 175.0 and 178.0 ppm of poly(MMA-BnMA)s obtained by PMAa to benzylation-methylation(a), methylation-benzylation (b)

PCA to extract information on primary structures

The resonance data of the four CH series (CH18 to CH65), seven AD series (AD12 to AD91), three SP series (SP50 to SP63), five TE series (TE23 to TE92), and two BM/MB series (BM57 and MB49) were combined to the reference dataset mentioned above, and the resulting dataset comprising the resonance data of total 41 samples was subjected to the PCA procedure. Figure 3.11 shows the score plots. The contribution rates for PC1 and PC2 changed to 72.4 % and 20.9 %, respectively, from the values described above. The increase of the contribution rate for PC2 from 12.6 % indicates the improvement of sensitivity to the monomer sequence analysis.

The plots of the CH series were found along the reference line for the homopolymer blends, suggesting that the copolymers prepared through the catalytic hydrogenolysis were of highly blocky natures. A study on Pd/charcoal-catalyzed cleavage of poly(benzyl acrylate) and PBnMA described that partial hydrogenolysis can lead to the formation of blocky copolymers or to mixtures of homopolymers depending on the structure of the Pd/charcoal catalytic system[33]. In the present study, the small differences between the CH series and the homopolymer blends in PC2 scores did not allow us to discriminate between highly blocky copolymers and mixtures of homopolymers. Because the multivariate analysis is a statistical approach, larger numbers of reference and sample data will be necessary to investigate these small differences.

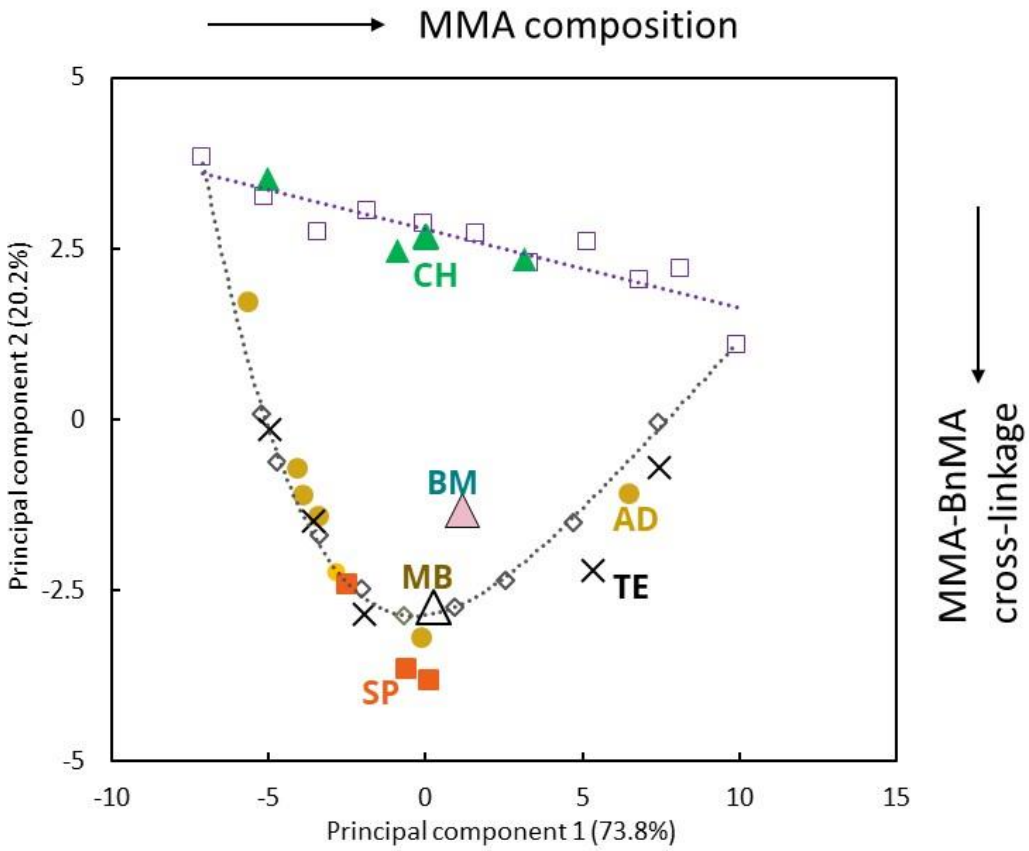
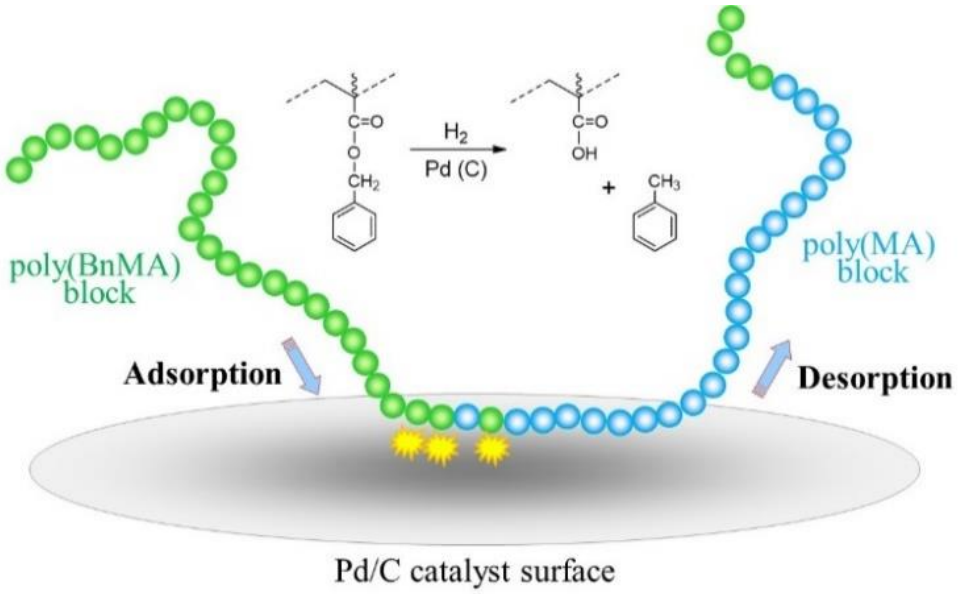


Figure 3.11. Principal component score plots for the α-methyl and carbonyl resonances of the MMA-BnMA copolymers obtained through the partial modifications of PBnMA by catalytic hydrogenation (CH series, ▲), acidic debenzylation (AD series, ●), saponification (SP series, ■), and transesterification (TE series, ×), and through two-step esterification of PMAa (BM57, ▲ and MB49, △). The reference framework of homopolymer blends and random copolymers is shown as the straight line and the parabolic curve accompanying small dot plots for H, B, and C series. The contribution rates for the first and second principal components (PC1 and PC2)

The fragmentation of PBnMA involved desorption immediately after the benzyl group was adsorbed onto the Pd/C catalyst (Scheme 3.2). Catalytic hydrogenolysis of this polymer was easy under mild conditions and the PMAa was easily recovered after filtering off the hydrogenation catalyst. The results of catalytic hydrogenolysis were

attributed to irregular reactions; nevertheless, the neighboring benzyl groups were converted to MAa groups because the desorption rate was not high. This probably explains why the monomer sequence from catalytic hydrogenolysis is blocky [33].

Scheme 3.2. The mechanism of catalytic hydrogenolysis.



The plots of AD91, TE92 and TE85 with positive PC1 values were found to be significantly below the parabolic curve for ideally random sequences, whereas the plots of the other samples for the AD and TE series with negative PC1 scores were distributed to almost lie on the parabolic curve. The neighboring group effects for promoting the formation of alternating sequences are suggested to have become prominent as the acidic debenzylation or transesterification of PBnMA proceeded to conversions higher than approximately 80 %. A similar tendency was observed for the plots of the SP series, where the formation of copolymers with alternating tendency was clearly indicated for SP59 and SP63. Unfortunately, the saponification of PBnMA did not proceed to conversions above 63 %.

The plot of MB49, a copolymer prepared by half methylation of PMAa with diazomethane followed by full benzylation with benzyl bromide in the presence of an organic base, was found on the parabolic curve. The result is in accordance with the publication reporting the formation of random copolymers in the partial methylation of syndiotactic PMAa with diazomethane [41]. The plot of BM57, obtained by half benzylation of PMAa followed by full methylation, was located significantly above the parabolic curve, indicating a somewhat blocky character of the monomer sequence. In the literature, however, the formation of random copolymers was claimed for the two-step esterification of highly syndiotactic PMAa under similar conditions [24]. A possible reason for the discrepancy is the difference of stereoregularity and the molecular weight of PMAa used in the esterification. Several papers mentioned the marked influence of stereoregularity and molecular weight on the reactivity of polymethacrylates[33,42-44].

Chapter 4 Quantitative Analysis Monomer Sequence of Isotactic and Syndiotactic poly(MMA-*co*-BnMA) prepared by Various Polymer Reactions

The atactic copolymers can be prepared by six reactions of catalytic hydrogenolysis, acidic debenzylation, Saponification and transesterification, respectively. The primary structures of monomer sequences obtained from polymer reactions can be analyzed by multivariate analysis *via* ^{13}C NMR spectra of poly(MMA-BnMA)s. However, quantitative analysis of monomer sequence of atactic copolymer was very difficult due to the complex chemical shift composition. High stereoregularity polymers will be a mean to solve to problem above. Hence, the quantitative determination of the sequence distribution is significant for the characterization of copolymers as well as the investigation on the mechanism of catalytic hydrogenolysis, acidic debenzylation and Saponification of highly stereoregular PBnMA (Figure 4.1).

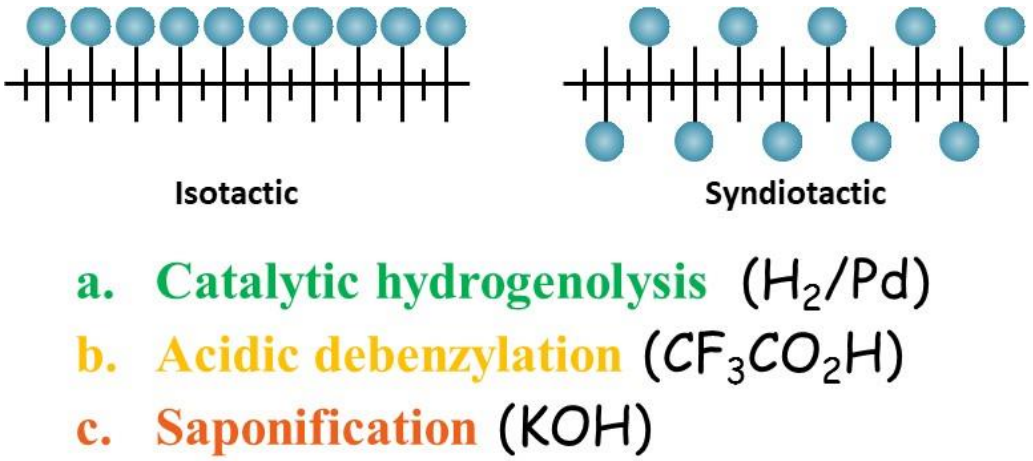


Figure 4.1. Various polymer reaction route of highly stereoregular PBnMA.

4.1 Characterization of Highly Isotactic PBnMA (*it*-PBnMA)

Isotactic-specific anionic polymerization of BnMA with initial *t*-BuLi l was carried out in toluene at −60 °C for 48 h [38,45]. The result are summarized in Table 4.1 The *mm*-triad content of this part was found to be 89.4% as determined by 500 MHz ^{1}H NMR spectroscopy.

Table 4.1. The anionic polymerization condition of *it*-PBnMA.

$\frac{t\text{-BuLi (mol)}}{\text{BnMA (mol)}}$	Toluene (ml)	Yield (%)	$M_n/10^4$ [a]	$\frac{M_w}{M_n}$ [a]	Tacticity (%) [b]		
					mm	*mr*	*rr*
0.03	5	99.1	1.6	3.8	89.4	8.3	2.3

[a] Determined by SEC using PMMA standards in Dimethylformamide (DMF).

[b] Determined by ^{13}C NMR in C_6D_6 at 75 °C.

Figure 4.2 illustrates the ^{13}C NMR spectrum of carbonyl group of region between 174 to 179 ppm of *it*-PBnMA of the polymer products obtained by anionic polymerization. The spectral pattern of the singlet centered at 176.2 ppm are due to the carbonyl carbon in *mmmm* configurational sequence.

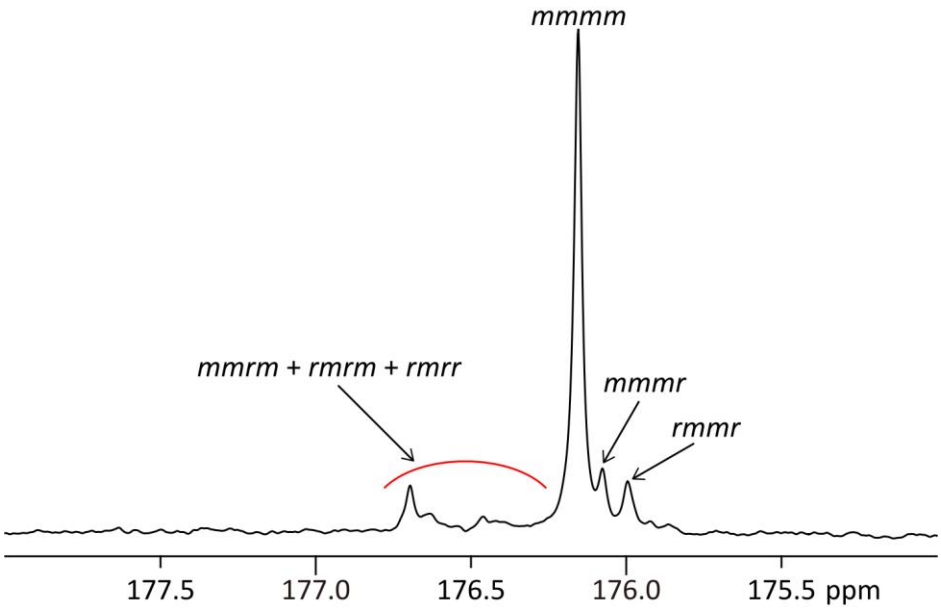


Figure 4.2. ^{13}C NMR spectrum due to the carbonyl group of region between 175.0 and 178.0 ppm of *it*-PBnMA. The measurement was performed in C_6D_6 at 75 °C.

4.2 Characterization of Highly Syndiotactic PBnMA (*st*-PBnMA)

The high syndiotactic PBnMA obtained from the anionic polymerization of benzyl methacrylate in toluene with initial *t*-BuLi and Et_3Al as catalyst at −78 °C for 72 h [46], the results of *st*-PBnMA and the ^{13}C NMR spectroscopy showed in Table 4.2.

Table 4.2. The anionic polymerization condition of high *st*-PBnMA.

$\frac{t\text{-BuLi (mol)}}{\text{BnMA (mol)}}$	$\frac{\text{Al}}{\text{Li}}$	Toluene (ml)	Yield (%)	$M_n/10^4$ [a]	$\frac{M_w}{M_n}$ [a]	Tacticity (%) [b]		
						mm	*mr*	*rr*
0.01	3	5	98.3	1.2	1.4	1.4	11.3	87.3

[a] Determined by SEC using PMMA standards in Dimethylformamide (DMF).

[b] Determined by ^1H NMR in 55 °C.

The *rr*-triad content of this part was found to be 87.3% as determined by 500 MHz ^1H NMR spectroscopy. Figure 4.3 illustrates the ^{13}C NMR spectra of *st*-PBnMA of carbonyl region and *α*-methyl group of the polymer products obtained by anionic polymerization. The spectral pattern of the three singlet centered at 177.1, 176.4 and 176.2 ppm are due to the carbonyl carbon in *rrrr*, *rmrr* and *mmmr* configurational sequence, respectively Figure 4.3 (a).

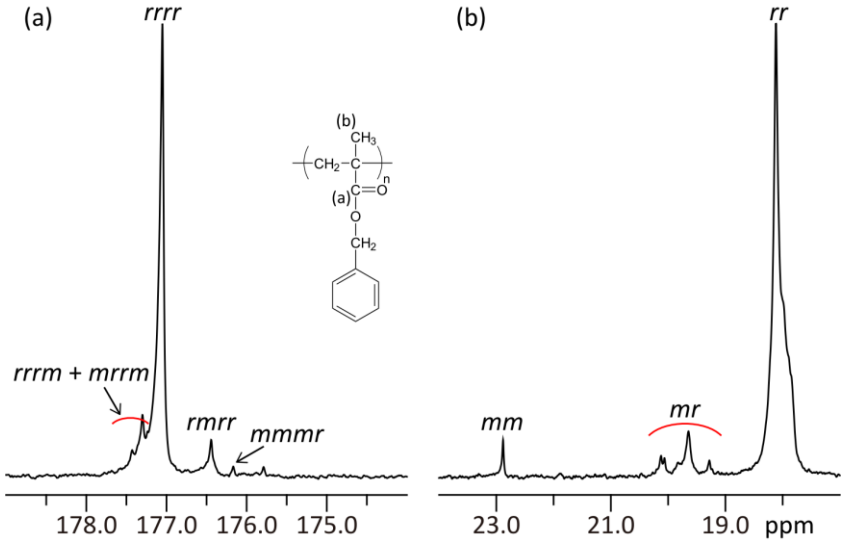


Figure 4.3. ^{13}C NMR spectra due to the carbonyl group and *α*-methyl group of *st*-PBnMA. The measurement was performed in C_6D_6 at 75 °C.

4.3 Catalytic Hydrogenolysis of Isotactic and Syndiotactic PbnMA

The *it*-, *st*-poly(MMA-*co*-BnMA)s derived from *it*-, *st*-PBnMA by catalytic hydrogenolysis with Pd/C followed by methylation with dizaomethane. For the resulting partially catalytic hydrogenolysis PBnMA, there are 4 possible triad sequences of the carbonyl region of the MMA and BnMA units. These are MBB, BBB, MMM and BMM where M and B denote the carbonyl region of the MMA and BnMA, respectively.

Figure 4.4 illustrates the ^{13}C NMR spectra of the carbonyl region of the polymer products obtained by subjecting *it*-PBnMA to catalytic hydrogenolysis (a) and *it*-homopolymer blend (b). The chemical shifts were observed at 176.4 and 176.2 ppm in the ^{13}C NMR spectrum in the Figure 4.4a. That corresponds to a sequence of MMM and BBB, respectively. This may support blocky distribution of *it*-poly(MMA-*co*-BnMA) derived from catalytic hydrogenolysis.

On the other hand, Figure 4.5 illustrates that ^{13}C NMR spectra of the carbonyl region of the polymer products obtained by subjecting *st*-PBnMA to catalytic hydrogenolysis (a) and *st*-homopolymer blend (b). The chemical shifts were observed at 177.19, 177.13, 176.65 and 176.58 ppm in the ^{13}C NMR spectrum in the Figure 4.4a. That corresponds to a sequence of BMM, MMM, BBB and MBB respectively. It is difficult to calculations between BMM and MMM or BBB and MBB because which overlap to give broad peaks. We estimated that the monomer sequence of the *st*-poly(MMA-*co*-BnMA) derived from *it*-poly(MMA-*co*-BnMA) was blocky.

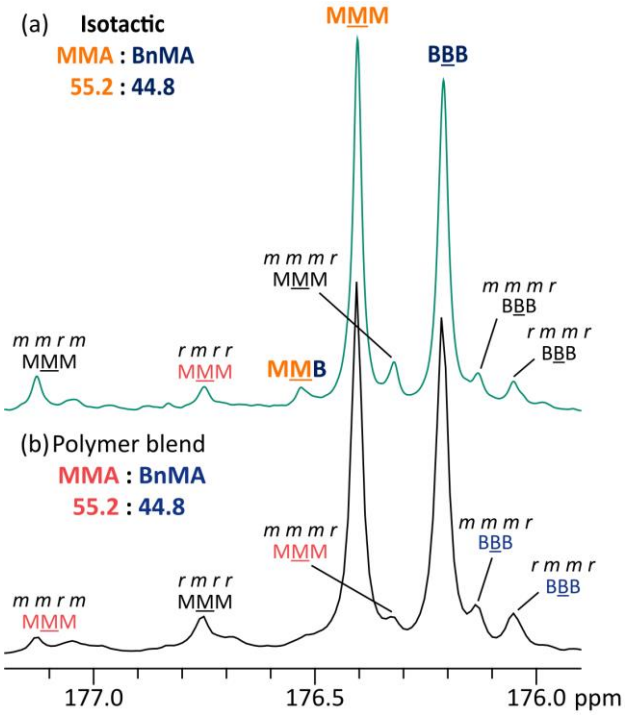


Figure 4.4. The ^{13}C NMR spectra in benzene-d_6 of the isotactic copolymer obtained by catalytic hydrogenolysis (green) (a) and homopolymer blend (black) (b).

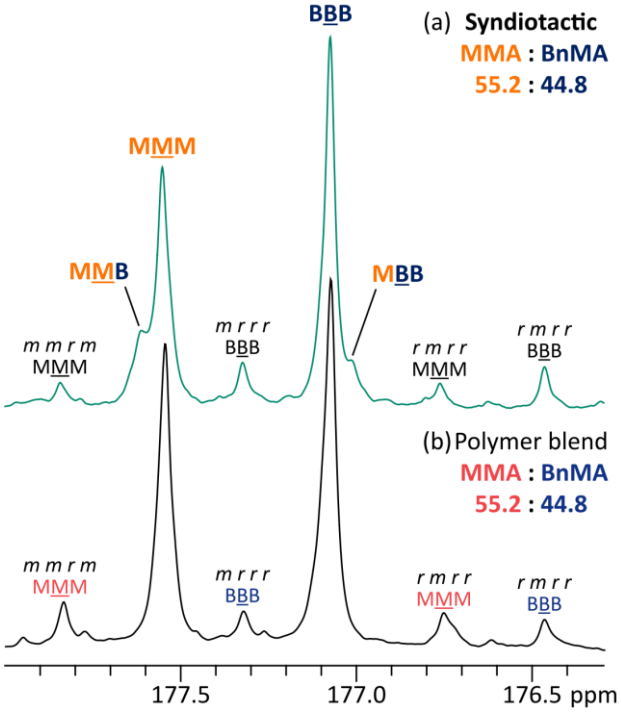


Figure 4.5. The ^{13}C NMR spectra of the *st*-poly(MMA-BnMA) obtained from catalytic hydrogenolysis (green) (a) and homopolymer blend (black) (b)

4.4 Acidic Debenzylation of Isotactic and Syndiotactic PbnMA

The *it*-, *st*-poly(MMA-*co*-BnMA)s were prepared through the acidic debenzylation followed by methylation. Figure 4.6 illustrates that ^{13}C NMR spectrum of the carbonyl region of the polymer products obtained by subjecting *st*-PBnMA to acidic debenzylation. The splitting of the resonances associated with the carbons in the carbonyl region can be attributed to the copolymer sequence. A complete analysis of these fine structures can potentially provide information about polymer composition. For the resulting partially acidic debenzylation PBnMA, there are 6 possible triad sequences of the carbonyl region of the MMA and BnMA units. These are, MBM, MBB, BBB, MMM, BMM and BMB where M and B denote the carbonyl region of the MMA and BnMA, respectively. The Figure 4.6 shows the region between 175.75 and 176.85 ppm of the *it*-poly(MMA-*co*-BnMA) obtained by subjecting *it*-PBnMA to from acidic debenzylation spectrum, where the 6 triads centered in the substituted units (MBM、MBB、BBB、MMM、MMB and BMB) can be observed. The persistence ratio (ρ) and average sequence length (L) of MMA and of BnMA units, L_M and L_B, calculated from the following formulas.

Table 4.3. The triad integral value and ρ value of carbonyl group of *it*-, *st*-poly(BnMA-*co*-MMA) obtained from partial Saponification.

Seteroregularity	Monomer sequence triads						L_B	L_M	ρ
	BMB	MMB	MMM	BBB	MBB	MBM			
Isotactic	12.0	26.4	19.8	5.90	19.2	16.7	2.31	1.59	1.06
Syndiotactic	13.8	30.3	19.1	14.0	9.40	13.5	2.18	2.03	0.95

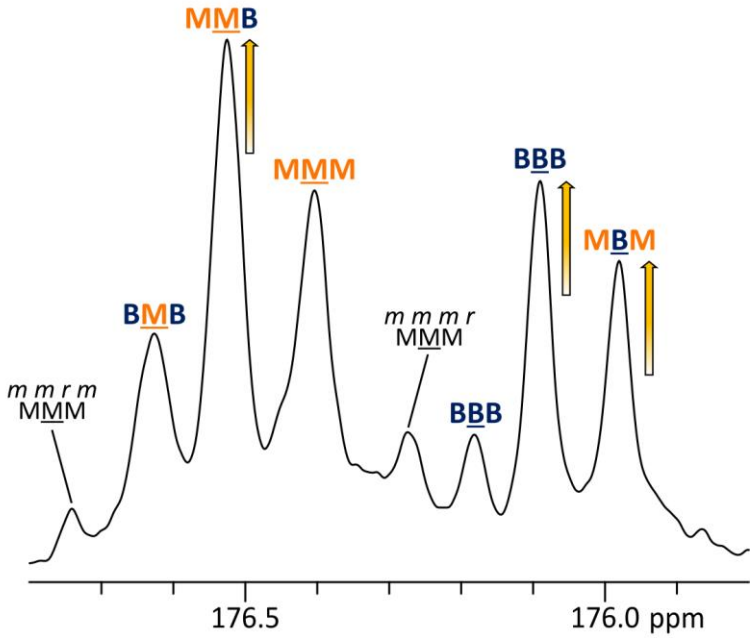


Figure 4.6. ^{13}C NMR spectrum of *it*-poly(MMA-*co*-BnMA) obtained from acidic debenzylation. The measurement was performed in C_6D_6 at 75 °C.

Persistence ratio (ρ)

$$\rho = \frac{1}{L_M} + \frac{1}{L_B} \begin{cases} \rho=0, \text{ Completely Blocky} \\ \rho=1, \text{Completely Random} \\ \rho=2, \text{ Completely Alternating} \end{cases}$$

Average sequence length (L)

$$L_M = \frac{I_{MMM} + I_{MMB} + I_{BMB}}{I_{BMB} + {}^{I_{MMB}}/_{2}} \quad L_B = \frac{I_{BBB} + I_{BBM} + I_{MBM}}{I_{MBM} + {}^{I_{BBM}}/_{2}}$$

The persistence ratio (ρ) value is a convenient guide to characterize a sequence distribution in binary copolymers; it take $0 \leq \rho < 1$ for blocky distributions, $\rho = 1$ for completely random cases, and $1 < \rho \leq 2$ for alternating cases. The polymer products obtained by subjecting *it*-PBnMA to from acidic debenzylation are close to random in distribution with $\rho = 1.06$.

On the other hand, the *st*-poly(MMA-BnMA) show overlapped splitting due to monomer sequences and configurational sequences in ^{13}C NMR spectrum, lead to not easily to analysis of these monomer sequence. It was possible to be determined the monomer sequence triads by ^{1}H NMR in DMSO-*d* (Figure 4.7). The chemical shifts between 3.3 and 3.7 ppm are due to the CH_3 in the MMA units), the signals located at 4.8-5.2 ppm (CH_2 in the BnMA units) of the ^{1}H NMR spectra. The *st*-poly(MMA-BnMA) prepared by acidic debenzylation , the sequence distributions are close to random with ρ = 0.95.

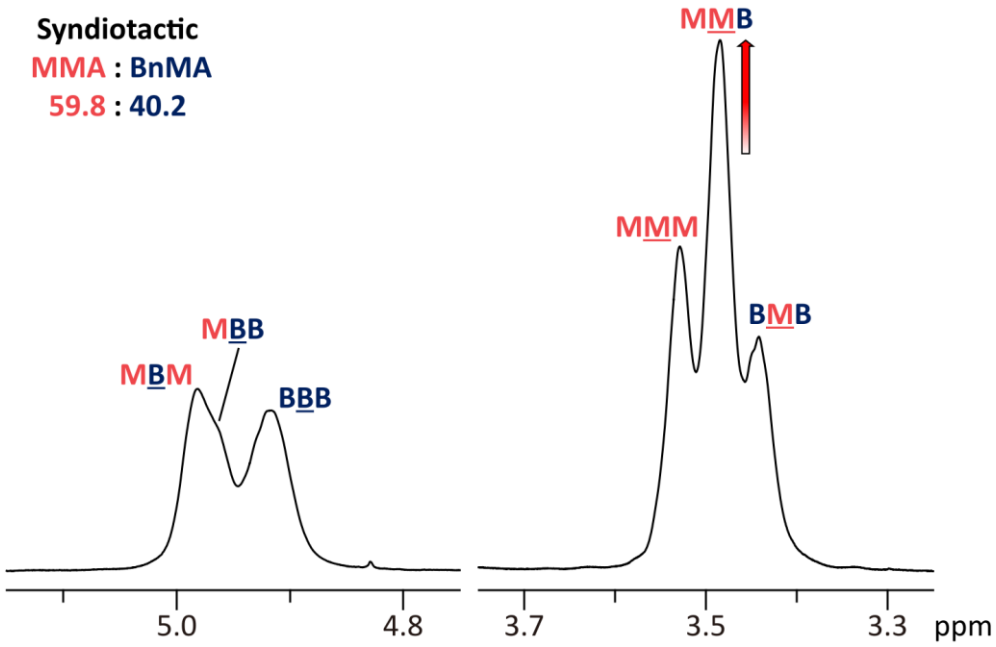


Figure 4.7. ^{1}H NMR spectra of *st*-poly(MMA-co-BnMA) obtained from acidic debenzylation. The measurement was performed in DMSO-*d* at 100 °C.

4.5 Saponification of Isotactic and Syndiotactic PBnMA

The use of phase transfer catalyst can increase the reactivity of Saponification. We used the 15-crown ether and 18-crown ether to compare the reactivity and the effect of tacticity on reactivity Figure 4.8 and Table 4.4. The reactivity of Saponification is strongly influenced by 18-crown ether than 15-crown ether. Because the K^+ ion of KOH is solubilized as a 1:1 complex with the 18-crown ether, the OH^- dissolved to maintain electroneutrality incidentally. In the other hand, result showed that *st*-PBnMA hydrolyze slowly, while the saponification of *it*-PBnMA proceeds very rapidly. The T*g* of PBnMA that isotactic lower than syndiotactic hence the isotactic polymer easier to react with KOH including 18-crown ether.

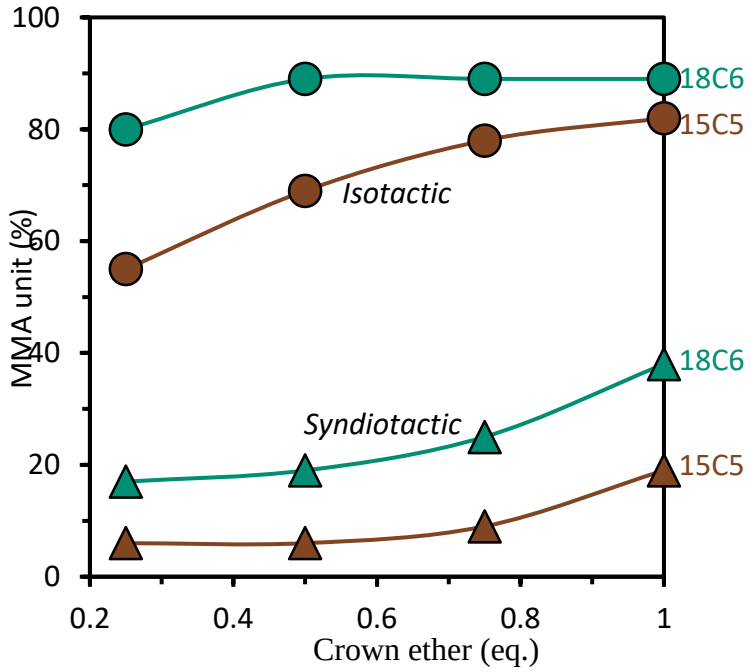


Figure 4.8. Reaction rare of Saponification of *it*-, *st*-PBnMA with 18-crown ether or 15-crown ether

Table 4.4. The experimental condition of partial Saponification of *st*-PBnMA.

Seteroregularity	Molar Ratio			Catalyst	Component *
	Reactant	Reagent	Catalyst	type	(BnMA / MMA)
Isotactic	1	15	0.25	15C5	45 / 55
Isotactic	1	15	0.5	15C5	31 / 69
Isotactic	1	15	0.75	15C5	22 / 78
Isotactic	1	15	1	15C5	18 / 82
Isotactic	1	15	0.25	18C6	20 / 80
Isotactic	1	15	0.5	18C6	11 / 89
Isotactic	1	15	0.75	18C6	11 / 89
Isotactic	1	15	1	18C6	11 / 89
Syndiotactic	1	15	0.25	15C5	94 / 6
Syndiotactic	1	15	0.5	15C5	94 / 6
Syndiotactic	1	15	0.75	15C5	91 / 9
Syndiotactic	1	15	1	15C5	81 / 19
Syndiotactic	1	15	0.25	18C6	83 / 17
Syndiotactic	1	15	0.5	18C6	81 / 19
Syndiotactic	1	15	0.75	18C6	75 / 25
Syndiotactic	1	15	1	18C6	62 / 38

* Determined by ^{1}H NMR signals, Solvent : $CDCl_3$.

The reaction temperature = 100 °C, Reaction time = 48 h.

Figure 4.9 illustrates that ^{13}C NMR spectrum of the carbonyl region of the polymer products obtained by subjecting *it*-PBnMA to Saponification spectrum, where the 6 triads centered in the substituted units (MBM、MBB、BBB、MMM、MMB and BMB) can be observed. The polymer products obtained by subjecting *it*-PBnMA to from acidic debenzylation are close to blocky in distribution with (ρ) = 0.67. The blocky of basic unit in partially hydrolyzed isotactic PBnMA suggests that ester groups are activated by neighboring hydrolyzed groups. Such neighboring group effects have been previously

reported in the base-catalyzed hydrolysis of methacrylate ester and in the hydrolysis of poly(vinyl acetate). The local chain conformation of isotactic PBnMA about a hydrolyzed monomer unit is presumably favorable for the hydrolyzed group to activate a neighboring ester group to yield a blocky copolymer.

Table 4.5. The triad integral value and ρ value of carbonyl group of *it*-, *st*-poly(BnMA-*co*-MMA) obtained from partial Saponification.

Seteroregularity	Monomer sequence triads						L_B	L_M	ρ
	BMB	MMB	MMM	BBB	MBB	MBM			
Isotactic	6.77	19.5	20.2	31.4	11.1	11.1	2.81	3.22	0.67
Syndiotactic	12.1	21.7	1.27	40.6	12.5	11.8	1.53	3.60	0.93

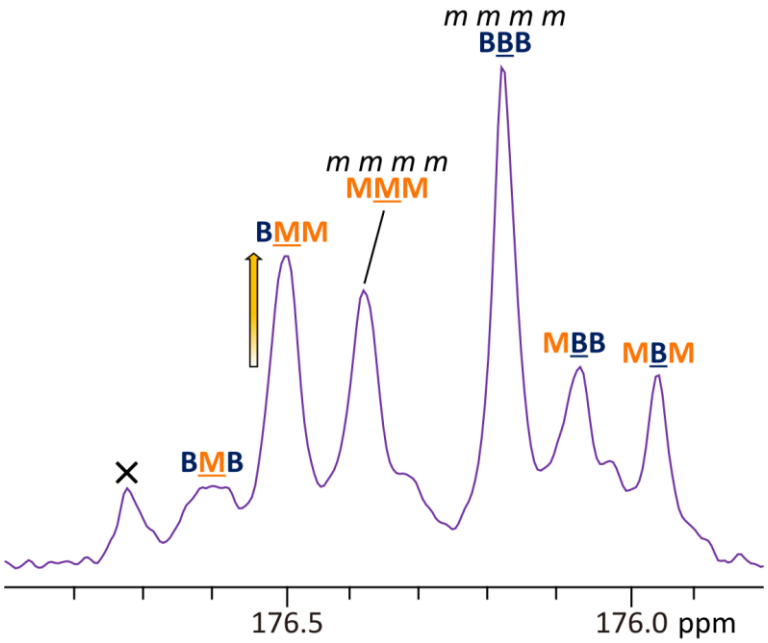


Figure 4.9. ^{13}C NMR spectrum of *it*-poly(MMA-*co*-BnMA) obtained from Saponification with KOH. The measurement was performed in C_6D_6 at 75 °C.

On the other hand, Figure 4.10 illustrates that ^{1}H NMR spectrum of the polymer products obtained by subjecting *st*-PBnMA to Saponification. The Saponification of *st*-PBnMA that hydrolyzed to only 35% in 48h at 85°C. The polymer products obtained by

subjecting *st*-PBnMA to from Saponification are close to random distribution with (ρ) = 0.93. We inferred that the *st*-poly(MMA-*co*-BnMA) have a somewhat alternating tendency with an increase in units of MMA.

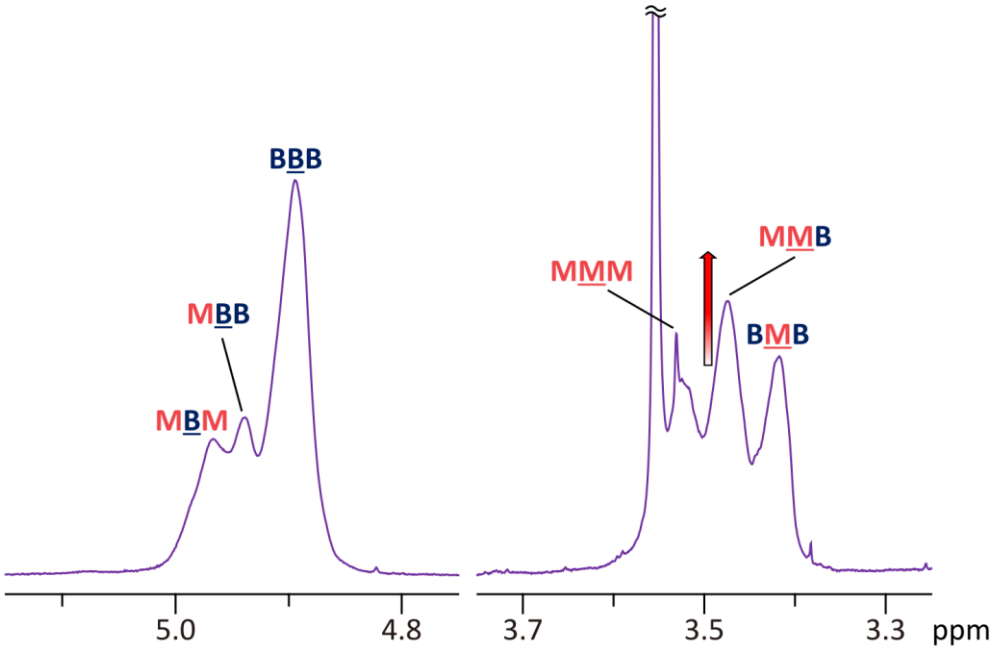


Figure 4.10. ^{1}H NMR spectrum of *st*-poly(MMA-*co*-BnMA) obtained from Saponification. The measurement was performed in DMSO-*d* at 100 °C.

The mechanism of crown ether react as phase transfer catalyst

The reaction rate of Saponification in this study were extremely slow due to the interfacial reaction, even if extend the reaction time, the conversion always below 3% of MMA component. One of the solution was finding an appropriate catalyst, crown ether showed the highly chemical affinity to K^+ [47]. First crown ether dissolved in toluene, crown ether in toluene will catch K^+ when K^+ on the o/w interface. K^+ which went through o/w interface dissolved into toluene phase, the reactivity will increasing at the same time, finally accelerated the overall reaction rate. (Figure 4.11)

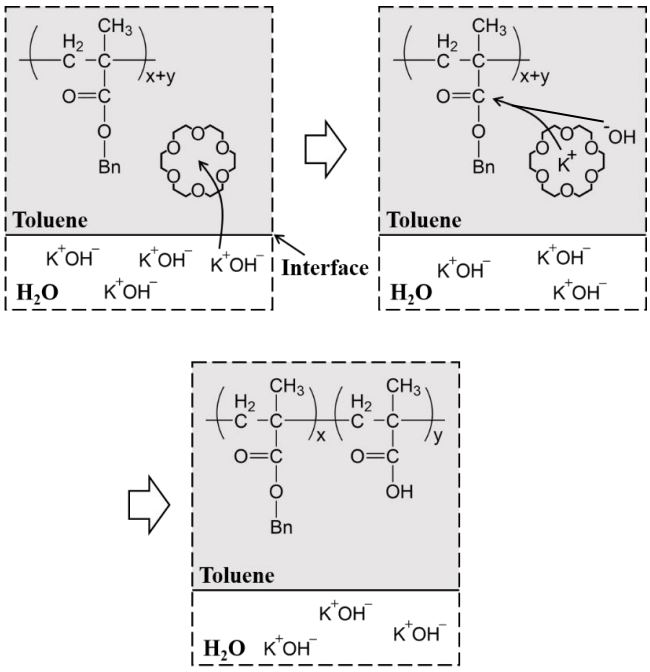


Figure 4.11. Mechanism of MAa obtained from PBnMA *via* Saponification in the presence of phase transfer catalyst.

Chapter 5 Conclusion

Copolymers were synthesized through six reactions, namely catalytic hydrogenolysis, acidic debenzylation, Saponification, transesterification, benzylation–methylation, and methylation–benzylation. Multivariate analysis of ^{13}C NMR spectra of poly(BnMA), poly(MMA), their blends, radical copolymers, and poly(MMA-BnMA)s through various reactions facilitated the characterization of the primary structures of monomer sequences. The PCA plots indicate that the monomer sequences in the copolymers synthesized through catalytic hydrogenolysis, acidic debenzylation, Saponification, and transesterification were highly blocky, random, somewhat alternating, and random with conversion to partially alternating with an increase in the content of MMA, respectively. Furthermore, the copolymers derived from benzylation–methylation and methylation–benzylation exhibited monomer sequences that were somewhat blocky and random, respectively.

Monomer sequence can be controlled by various polymer reaction. Including the catalytic hydrogenolysis, acidic debenzylation, Saponification and transesterification. Monomer sequence analysis of atactic copolymers by multivariate analysis was possible. Quantitative analysis of monomer sequence can be carried out on copolymers with high stereoregularity. The finding of this work are possible to be used in the development of new sequence controlled polymers.

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