Analysis of Compositional Drift in Methyl Methacrylate and *n*-Butyl Acrylate Copolymers Synthesized by Atom Transfer Radical Polymerization Using $^{13}\text{C}\{^1\text{H}\}$ NMR Spectroscopy

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ABSTRACT: Compositional variations occurring along the chains in the copolymers of methyl methacrylate (M) and *n*-butyl acrylate (B) were investigated using $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Copolymerization of methyl methacrylate and *n*-butyl acrylate with varying infeed ratio was done using Atom Transfer Radical Polymerization. Copolymer compositions were determined from ^1H NMR spectra. Percentage conversion was studied gravimetrically. Analysis of the variations of β methylene dyads fractions and M- and B-centered triad fractions with conversion was done using Distortionless Enhancement by Polarization Transfer (DEPT) experiments to have a better insight to trend followed by the compositional drift with conversion. The experimental results were found to be in good agreement with the simulated data indicating towards the uniformity along the copolymer chains resulting in the formation of gradient copolymers. [DOI 10.1295/polymj.37.316]

KEY WORDS Atom Transfer Radical Polymerization (ATRP) / Methyl Methacrylate / *n*-Butyl Acrylate / Gradient Copolymers / NMR /

Synthesis of well-defined polymers has always been an area of interest in polymer chemistry. The architecture and composition of the copolymers play a vital role as they greatly influence the physical properties. Hence, the knowledge about the composition and distribution of monomer units along the macromolecular chain is very important to correlate structure–property relationship.^{1,2}

With the introduction of the concept of controlled/living radical polymerization, control over molecular weight, polymer structure and composition has enabled to synthesize well-defined polymers.³ In this direction, Atom Transfer Radical Polymerization (ATRP) has been successfully utilized.^{4,5} Besides having the advantages of free-radical polymerization, ATRP also provides a way to synthesize novel materials having well-defined compositions and different types of architecture such as block copolymers, star polymers, end-functionalized polymers, etc.^{6–8} Being a versatile method, it is applicable to a wide range of monomers. A lot of work has been carried out on methacrylate and acrylate monomers as their copolymers find vast applications in industries ranging from being used as adhesives, sealants etc to high band width optical fibers. Recently, there have been reports on the synthesis of gradient copolymers by ATRP.^{9–16}

Reactivity ratios and monomer infeed ratio play an important role in determining the structure of the copolymers.¹⁷ In conventional radical polymerization, difference in the reactivity ratios of the monomers

lead to variation of composition among the polymer chains. In controlled/living radical polymerization, due to slow initiation and negligible termination, essentially every chain survives from the very beginning to the final stage of polymerization. Any variation of the monomer feed along with reactivity ratio differences results in difference in the rates of incorporation of the monomer. Therefore, changes in the instantaneous composition arising from these variations are reflected along the chains. This leads to the formation of gradient copolymers.^{9,10} These copolymers act as a connecting link between random statistical copolymers where compositional variation is seen among the chain and block copolymers which show variation in composition in regular fashion among the chains.

NMR is a powerful and versatile technique to study the microstructure of polymers.^{18,19} High resolution NMR is particularly effective in the study of structural and sequence details of the polymers. It provides the quantitative analysis on the sequence distribution of the polymers as the chemical shifts are both configurational and compositional sensitive.²⁰

In ^1H NMR, the chemical shift difference between the various proton nuclei, which are in the different compositional and configurational environment, is usually small leading to broad and overlapping signals. In case of $^{13}\text{C}\{^1\text{H}\}$ NMR, the signals obtained from carbon in structurally unique environment have intensities proportional to the number of resonating nuclei. Moreover, due to the large chemical shift

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ranges, the effect of comonomer sequence on the chemical shift is observable. The spectra are rich in the information regarding comonomer sequence.

Matyjaszewski *et al.* have prepared copolymers of methyl methacrylate (M) and *n*-butyl acrylate (B) using ATRP catalyzed by three different catalyst systems.⁹ By studying the change in copolymer composition with conversion, they have concluded that gradient copolymers have been formed.

Madruza *et al.* have studied the sequence distribution and stereoregularity of methyl methacrylate and *n*-butyl acrylate copolymers both in bulk and in benzonitrile solution.²¹ They have carried out studies on two copolymer series using CuCl/bpy as the catalyst systems with two different initiators at 100 °C. They have analyzed the carbonyl region of these copolymers by studying the relative intensity dependence of the monomer triad fractions as a function of conversion. They have concluded that the copolymer composition and microstructure is independent of the controllability of ATRP.

Brar *et al.* have reported the complete spectral assignments for the microstructure of methyl methacrylate and *n*-butyl acrylate copolymers synthesized by ATRP using 2D NMR spectroscopy.²²

In this report, investigation of carbon resonances of β -methylene of methyl methacrylate (M) and *n*-butyl acrylate (B), methine of *n*-butyl acrylate (B) and α -methyl of methyl methacrylate (M) of the M/B copolymers synthesized by ATRP was done using $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. CuBr/PMDETA with methyl 2-bromopropionate as the initiator was used in ATRP at 60 °C. Entire conversion range was studied. The variation of dyad and triad fractions obtained from DEPT experiments with conversion was analyzed to have a better insight to compositional drift occurring along the chains of copolymer.

EXPERIMENTAL

Materials

Methyl methacrylate (M) (Merck, 98%) and *n*-butyl acrylate (B) (Merck, 98%) were dried over CaH_2 , vacuum distilled and kept below 5 °C before use. Methyl 2-bromopropionate (MBP) (99%, Aldrich) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) (99%, Aldrich) were vacuum-distilled prior to use. Copper Bromide (CuBr) (99.99%, Aldrich) and Copper powder (99%, CDH) were used as received.

Polymerizations

Copolymerization of methyl methacrylate and *n*-butyl acrylate was carried out in three different infeed ratios 0.3:0.7, 0.5:0.5, and 0.7:0.3 under ATRP

conditions. The molar ratio for ATRP were taken as $[\text{Monomer}]:[\text{MBP}]:[\text{CuBr}]:[\text{Cu(0)}]:[\text{PMDETA}] = 100:1:1:0.5:1$. In a typical procedure, a stock solution containing the calculated amount of the methyl methacrylate and *n*-butyl acrylate along with methyl 2-bromopropionate and PMDETA was prepared. The system was degassed by three vacuum-nitrogen cycles and then sealed with septum. The boiling tubes containing the calculated amount of CuBr and Cu(0) were purged with N_2 prior to sealing with septum. To these boiling tubes, 10 mL of stock solution was added *via* syringe and then kept in the oil bath at 60 °C. Progress of the polymerization was followed by cooling the boiling tubes to room temperature and then dissolving the solution in chloroform. The polymers were dried to constant weight in vacuum oven at 30 °C. These polymers were redissolved in chloroform and precipitated in methanol/water (1:1).

Characterization

Percentage conversion was measured gravimetrically. The molecular weight (M_n) and the polydispersity index (M_w/M_n) of these copolymers were measured using Gel Permeation Chromatography (GPC) equipped with a Waters 501 pump with guard column and a Waters 410 RI detector against polystyrene standards. Copolymer compositions were calculated from ^1H NMR spectra. All the spectra were recorded on Bruker DPX-300 spectrometer in CDCl_3 at frequencies of 300.13 MHz and 75.5 MHz for ^1H and ^{13}C , respectively at 25 °C. A delay time of 10 s was given for recording ^1H NMR spectra while for $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, 2 s delay time was given and 4 K scans were accumulated. DEPT-45, 90, 135 spectra were recorded using standard pulse sequence with *J* modulation time of 3.7 ms ($J_{\text{CH}} = 135 \text{ Hz}$) with a delay time of 2 s the signal intensities of the spectra peak were measured from the integrated areas calculated with electronic integrator. Measurements were made on 10% (w/v) polymer solutions of various compositions at different conversion as given in Table I.

Reactivity Ratios and Simulations

For polymerization involving high conversion, calculation of reactivity ratios by low conversion method, *i.e.*, by Kelen–Tudos method becomes incorrect.^{23,24} Therefore, reactivity ratios were optimized by the methodology described previously.^{22,25} The copolymer compositions F_M were theoretically calculated using equation,

$$F_M = \frac{r_M f_M^2 + f_M f_B}{r_M f_M^2 + 2f_M f_B + r_B f_B^2}$$

Simulation of F_M with percentage conversion for the copolymerization of M and B with reactivity ratios

Table I. NMR measurements on the polymer samples synthesized by ATRP having different composition at different conversion along with reaction time and experimentally determined dyad and triad fractions

f_M M/B	Reaction time (min)	F_M	% Conv	MM/MB/BB	BBB/BBM/MBM	MMM/BMM/BMB
0.3/0.7	65	0.46	23	0.27/0.52/0.22	0.27/0.49/0.23	0.20/0.49/0.30
0.3/0.7	125	0.43	45	0.33/0.49/0.17	0.31/0.48/0.20	0.17/0.48/0.35
0.3/0.7	155	0.41	57	0.34/0.52/0.14	0.34/0.48/0.19	0.16/0.46/0.36
0.3/0.7	215	0.36	80	0.43/0.45/0.13	0.42/0.45/0.16	0.13/0.43/0.46
0.3/0.7	250	0.32	93	0.48/0.42/0.11	0.50/0.40/0.10	0.11/0.40/0.52
0.5/0.5	50	0.65	21	0.10/0.45/0.44	0.10/0.43/0.46	0.42/0.45/0.12
0.5/0.5	80	0.64	39	0.13/0.47/0.40	0.12/0.45/0.41	0.40/0.46/0.14
0.5/0.5	140	0.60	54	0.15/0.48/0.38	0.14/0.46/0.40	0.38/0.47/0.16
0.5/0.5	200	0.56	76	0.19/0.48/0.34	0.18/0.48/0.34	0.32/0.48/0.22
0.5/0.5	310	0.51	93	0.24/0.47/0.29	0.25/0.46/0.30	0.28/0.44/0.28
0.7/0.3	55	0.84	20	0.03/0.32/0.66	0.03/0.20/0.71	0.68/0.29/0.03
0.7/0.3	115	0.82	45	0.05/0.30/0.64	0.03/0.30/0.66	0.65/0.31/0.04
0.7/0.3	145	0.80	63	0.04/0.32/0.63	0.05/0.32/0.67	0.64/0.32/0.04
0.7/0.3	175	0.77	79	0.05/0.45/0.60	0.05/0.32/0.63	0.62/0.32/0.03
0.7/0.3	290	0.70	95	0.09/0.39/0.53	0.09/0.35/0.55	0.54/0.36/0.10

$r_M = 2.17$ and $r_B = 0.42$ was done using Microsoft Excel Worksheet. The steps used in simulation to find the copolymer composition were:

- Taken $r_M = 2.17$ and $r_B = 0.42$, infeed mole fraction $f_M = 0.485$ and total no of moles = 100 moles.
- F_M is calculated using the above equation for 0.01% conversion in each step, new infeed of M and B are calculated for the next step.
- The cycle of step ii was repeated until 100% conversion has been achieved.

Simulations for monomers centered dyad and triad fractions were calculated using the copolymer composition data, conversions and reactivity ratios of 2.17 and 0.42 for methyl methacrylate and *n*-butyl acrylate, respectively. The reaction probabilities were calculated from the reactivity ratios using the following equations,

$$p_{AA} = \frac{r_A}{r_A + ([M_B]/[M_A])}; \quad p_{AB} = 1 - p_{AA}$$

$$p_{BA} = \frac{1}{1 + r_B([M_B]/[M_A])}; \quad p_{BB} = 1 - p_{BA}$$

where, M_A and M_B are the infeed fractions of A and B monomers, respectively. p_{AA} , p_{AB} , p_{BA} and p_{BB} are the reaction probabilities. p_{AA} and p_{AB} are the probabilities of A and B monomer units, respectively getting attached to the A radical at the growing chain end.

The intensities of AA, AB/BA and BB dyad fractions are calculated from the outfeed monomer fraction of the first monomer depicted in the dyad and

the probability of second monomer following it. The dyads fractions are calculated as shown:

$$F_{AA} = F_A p_{AA}; \quad F_{AB} = F_A p_{AB};$$

$$F_{BA} = F_B p_{BA}; \quad F_{BB} = F_B p_{BB}$$

The monomer centered triad fractions are calculated as the multiplication of the probabilities of the outer monomer units following the central monomer unit, given as:

$$F_{AAA} = (p_{AA})^2; \quad F_{BAA} = 2(p_{AB})(p_{AA}); \quad F_{BAB} = (p_{AB})^2$$

$$F_{BBB} = (p_{BB})^2; \quad F_{ABB} = 2(p_{BA})(p_{BB}); \quad F_{ABA} = (p_{BA})^2$$

The dyad and triad fractions were calculated using the above equations for 0.01% conversion. This cycle was repeated till 100% conversion was achieved.

RESULTS AND DISCUSSION

Three different series of methyl methacrylate/*n*-butyl acrylate (M/B) copolymers were synthesized by ATRP. For each series, [Monomer]/[Initiator] ratio was taken 100:1. In the bulk copolymerization, linear increase in M_n was observed with decrease in PDI as conversion progressed. Figure 1 shows the variation of M_n and PDI with conversion for the three feed compositions.

The copolymer compositions for the three feed compositions involving conversion were determined from the ^1H NMR spectra of the copolymers from the relative intensities of the signals of the methoxy

Figure 1. Variation of M_n and PDI with conversion in M/B copolymers synthesized under ATRP conditions.

protons of M unit and oxy methylene protons of B unit in the ^1H NMR spectrum using the following expression:

$$F_M = \frac{I(\text{OCH}_3)/3}{I(\text{OCH}_3)/3 + I(\text{OCH}_2)/2}$$

where, $I(\text{OCH}_3)$ is the area under the resonance signal of (OCH_3) protons of M unit, $I(\text{OCH}_2)$ is the area under the resonance signal of (OCH_2) protons of B unit and F_M is the mole fraction of M unit in the copolymer.

The reactivity ratios of the monomers were obtained from the compositions of copolymers with conversion using the methodology described previously.²² The values obtained are $r_M = 2.17$ and $r_B = 0.42$. The differences found in the monomer reactivity ratios with those reported in the literature^{9,21} for this system might be due to the different copolymerization temperature and initiator/catalyst system. Figure 2 shows the copolymers composition, F_M as a function of conversion. The experimental values are consistent with these reactivity ratios of the monomers. The good agreement between the theoretical and the experimental F_M indicates that the active species formed in ATRP has the same chemoselectivity as for the car-

Figure 2. Variation of copolymer composition (F_M) as a function of conversion. The solid line represents the simulation. Solid symbols represent copolymer composition obtained in bulk.

bon centered free radical generated in conventional radical polymerization.

For the three feed compositions (Figure 2), the trend followed by F_M as the function of conversion is the same indicating that there is a significant continuous change in the copolymer composition with conversion. The composition of the copolymer formed from a particular feed composition at high conversion is different from the copolymer composition at low conversion. The comonomer feed changes in composition as one of the monomer preferentially enters the copolymer chain. Thus, there is a drift in the comonomer composition towards the less reactive monomer as the degree of conversion increases. This results in the similar variation of copolymer composition with conversion. When the reactivity ratios of the monomers vary significantly and along with this factor, variation of monomer infeed is incorporated then the properties of the copolymer become conversion dependent.

For each tactic sequence distribution, both the monomer reactivity ratios and monomer feed fractions is important. Because the monomer reactivity ratios values are different (the difference is of more than one unit), the monomer feed composition varies with conversion, resulting in the change in the monomeric sequence distribution along the main chain during the copolymerization. The correlation of the molar concentration of M- and B-centered sequences with conversion will give a clear picture of the compositional drift occurring along the chains. In order to confirm this, analysis of the M-centered and B-centered dyad

and triad fraction concentrations, obtained from $^{13}\text{C}\{^1\text{H}\}$ NMR and DEPT with conversion was done.

The methine, methylene, α -methyl and carbonyl carbon resonances of the M/B copolymers are compositional sensitive. So, the variation in composition will be reflected in the concentrations of the dyad and triad fractions along with conversion.

Both M and B contain carbonyl carbons, and since their resonances overlap, the resonance patterns of the carbonyl carbon resonances in M/B copolymers are complicated combination of both M-centered and B-centered triad fractions. Since our aim is to study the compositional drift reflected in the concentrations of the dyad and triad fractions along with conversion, such type of overlap and complexity was ignored. The same information regarding various M-centered and B-centered triad sequences are obtained in a very clear manner from the α -methyl and methine carbon resonances of the M/B copolymers, respectively. Since these regions are well resolved, calculation of the concentration of the triad fractions becomes less erroneous.

The concentration of various M and B-centered dyad and triad fractions was calculated from the relative areas of the resonance signals (Table I). These concentrations are normalized areas of the respective resonance sequences.

The most explicit picture of the compositional drift with conversion is depicted in the methine carbon resonance pattern obtained from DEPT-90 of M/B copolymers, which is sensitive to B-centered triad compositional sequences. Figure 3 shows the methine region for $F_M = 0.50$ with conversion. B-centered tri-

Figure 3. DEPT-90 NMR spectra showing the methine region of M/B copolymers for $F_M = 0.50$ at (a) 0.21 (b) 0.54 and (c) 0.93 conversion.

ad distributions are divided into three resonance areas centered in BBB, BBM + MBB and MBM. The assignments are done according to Brar *et al.*²² and Harwood *et al.*²⁶ It is observed that as the conversion increases, the intensities of the signals assigned to MBM triad and BBM + MBB triads decreases. The reactivity ratio of M is higher than B, so the probability of addition of M to the copolymer chain is more. This leads to increase in the content of B at later stages of conversion. Since all the chains essentially survive from the initial stages to the final stage of polymerization, any variation in the monomer infeed will be reflected in the triad concentrations and as a result the decrease in the intensities is observed with conversion.

In order to get a better insight, plots of the B-centered triad concentrations for the three infeed compositions were studied as a function of conversion (Figure 4). The simulated and the experimental data agree well with each other. For BBM triad fraction (Figure 4b), one can clearly see the difference in the trend followed by the three infeed ratios. For the $f_M = 0.48$, there is an increase in the concentration till 80% conversion after which a gradual decrease is observed as the M content is negligible at final stage of conversion. As the polymerization proceeds, a gradual decrease in the concentration of BBM triads is observed for $f_M = 0.29$. In BBB triad fraction (Figure 4a), for all infeeds, there is a gradual increase in the concentrations with conversion. Similarly, for MBM triad fractions as seen in Figure 4c, the decrease in concentration is very gradual for $f_M = 0.70$ but it almost linear for $f_M = 0.29$.

The α -methyl resonance of methyl methacrylate in M/B copolymers obtained from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra consists of three resonance areas assigned to M-centered triads²³ as shown in Figure 5. These are MMM, BMM + MMB and BMB triads. The MMM region can be further splitted into configurational sensitive triads, *i.e.*, rr-MMM, (mr + rm)-MMM and mm-MMM. The (mr + rm) MMM region contains some residual peak of the side chain CH_2 of B unit. For the calculation of the concentration of MMM triad fraction, a different approach was utilized. The concentration for MMM triad fraction was calculated from the isotactic parameter²³ and the area under the resonance rr-MMM.

From the study of F_M as a function of conversion, the conclusion drawn was that there is a continuous and significant decrease in the content of M as the chain length increases. Since these triad fractions are M-centered, one of the expected observations will be decrease in the concentrations as the conversion increases. This is clearly visible in Figure 6 where a gradual decrease occurs for all the infeed composition

Figure 4. Variation of B centered triad fractions as a function of conversion where (a) BBB (b) BBM and (c) MBM. The solid lines are based on calculations made using $r_M = 2.17$ and $r_B = 0.41$ while solid symbols represent experimental data.

Figure 5. Expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showing the α -methyl region of M/B copolymers for $F_M = 0.50$ at (a) 0.21 (b) 0.54 and (c) 0.93 conversion.

Figure 6. Variation of M centered triad fractions as a function of conversion where (a) MMM (b) MMB/BMM and (c) BMB. The solid lines are based on calculations made using $r_M = 2.17$ and $r_B = 0.42$ while solid symbols represent experimental data.

for MMM and BMB triads. Here also, experimental data is in agreement between the simulated data.

The backbone methylene carbon resonances of the M/B copolymers, obtained as subspectra of DEPT-45 and DEPT-135 are dyad sensitive. This region also contains some residual peak of quaternary carbon of M unit. Figure 7 shows the three envelopes of dyad fractions, that is. MM, MB/BM and BB.²³ The variation of these dyad concentrations for the three infeed with conversion is shown in the Figure 8. The trend followed by these fractions is the expected one indicating that there is indeed a uniform and continuous drift occurring in the composition as the conversion goes on.

The results shown by the study of M-centered and B-centered dyad and triad fractions with conversion for three different series indicate that these copolymers show the compositional drift occurring along

Figure 7. DEPT subspectra showing the backbone methylene region of M/B copolymers for $F_M = 0.50$ at (a) 0.21 (b) 0.54 and (c) 0.93 conversion.

Figure 8. Variation of dyad fractions as a function of conversion where (a) BB (b) BM/MB and (c) MM. The solid lines are based on calculations made using $r_M = 2.17$ and $r_B = 0.42$ while solid symbols represent experimental data.

the chain, *i.e.*, gradient copolymers can be synthesized using ATRP when the monomer reactivity ratio difference is large.

CONCLUSIONS

Linear increase in M_n and low polydispersity showed the controlled character of the polymerization. The variation of copolymer composition (F_M) with conversion indicated towards the synthesis of copolymers having significant continuous change in the composition with conversion. Further confirmation was done by studying the variation of various M-centered and B-centered dyad and triad fraction concentration with conversion. The compositional trend shown by these fractions was similar demonstrating that indeed uniformity in copolymer chains is there resulting in the formation of gradient copolymers by Atom Transfer Radical Polymerization. The simulated and experimental data were in agreement with each other.

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