NMR Study of Polyacrylamide Tacticity Synthesized by Precipitated Polymerization Method

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A B S T R A C T

In this study polyacrylamide was prepared in various molar ratio contents of ethyl acetate and ethanol at 60ºC by free-radical precipitated polymerization method. The assignment of all stereosequences at pentad level of methine, hexad level of methylene, and triad level of carbonyl carbons of the polyacrylamide were observed using ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR) in deuterium oxide at room temperature. Bernoullian and 1st-order Markov statistics were used for all carbons and the results were compared with experimental data by statistical method. It was shown that Bernoullian statistics model fit slightly better than 1st-order Markov statistics model for the assigned sequences. The results indicated that corresponding values of the probability (P_m) and length average (N_m) of meso addition were 0.443 and 1.698, respectively and no significant differences were observed by changing the molar ratios of the two solvents. By heteronuclear multiple quantum coherence (HMQC) as two-dimensional NMR spectroscopy, the methylene and methine groups were assigned by triad sequences in which isotactic contour was thoroughly isolated from syndiotactic and atactic contours. Therefore, isotactic triad sequence could only be calculated by ^1H NMR. In other words, isotactic placement value was calculated by using the integration of areas of methylene and methine protons (mm = 0.21) peaks.

INTRODUCTION

Precipitated polymerization is a kind of semi-homogenous polymerization that as soon as polymer is formed, it precipitates from its solvent. In this system, all components, e.g., monomer, initiator, and solvents form a homogeneous phase at the beginning of the reaction. But, after polymer chain formation two phases are emerged as precipitated polymer chains and diluents (continuous phase). Therefore, precipitated polymerization could belong to classification of heterogeneous or multiphase polymerization. Precipitated polymerization mechanism is similar to that of suspension polymerization where each particle acts as a reactor and polymerization reactions take place in the particles [1-3].

Tacticity and stereocontrol are very essential during free-radical polymerization, for they are broadly used for producing a variety of polymers in industry and their properties are often influenced

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considerably by stereoregularity. In the reports, stereocontrol for polymer chains, coordination, and ionic polymerization methods have been studied. However, it is generally quite difficult to control the tacticity in free-radical polymerization systems and only a few stereospecific reactions have been studied [4-9]. In the last decade, various techniques have been adopted in radical polymerization processes. In addition, in conventional free-radical polymerization methods, there are living radical polymerizations such as nitroxide-mediated polymerization (NMP) [11-12], atom transfer radical polymerization (ATRP) [13-15] and reversible addition fragmentation chain transfer (RAFT) [16-18], which are useful and efficient approaches to control stereoregularity [19-22]. Among these methods, ATRP is perhaps the most desirable mechanism in controllability, facility, and adaptability. ATRP is used for wide varieties of vinyl monomers with various types of initiators and catalysts and provides the opportunity of synthesizing homopolymers and copolymers with different stereochemistry [23].

One of the most popular studies on the microstructure is performed on polyacrylamide. Polyacrylamide and its derivatives are a kind of water-soluble polymers with various applications that can be only polymerized by free-radical polymerization, due to the limitation of their acidic amide proton and stereocontrol parameters. Therefore, the expansion of an effective and simple stereocontrol method is essential in the area of polymer chemistry and industry [24-27]. Some researchers have studied the polyacrylamide tacticity and microstructure in free-radical polymerization by bulk and solution polymerization methods [28-30]. Use of solvents and Lewis acids as ingredient materials in polymerization of acrylamide can be efficient on tacticity [31-33]. Habaue et al. [33] have widely studied the conventional free-radical polymerization of acrylamide in various solvents (such as water, dimethyl sulphoxide, methanol, tetrahydrofuran, and chloroform) and with use of Lewis acids (such as ytterbium and yttrium trifluoromethanesulphonate). They have concluded that isotactic part of polyacrylamide chains would be increased by using methanol as solvent and Lewis acid.

One of the best analytical methods for tacticity

determination of polymers and copolymers is ^{13}C NMR [34-37]. In some of the papers, ^{1}H NMR has been used for determination of polyacrylamide microstructure [22], but due to expansion of ^{13}C NMR spectrum sweep width, peaks can be split by higher resolution. Hikichi et al. [38] have extensively considered tacticity of polyacrylamide prepared in solution media by 1D and 2D NMR spectroscopy techniques. They have concluded that polymerization of polyacrylamide in aqueous solution proceeds in a Bernoullian statistical model with near to ideal atactic stereoregularity.

In this work, tacticity study of synthesized polyacrylamide by precipitated polymerization method has been considered in various molar ratio contents of solvents; there is not any report about it. In addition, by using various NMR techniques, microstructure of polymer chains have been studied and tacticities on carbon and proton nuclei are determined, and for quantitative agreement data have been used from Bernoullian and 1st-order Markov statistical models. Analysis of either methylene and methine protons or methylene, methane, and carbonyl carbons were studied By ^{1}H NMR and ^{13}C NMR spectroscopy techniques, respectively. Triad sequence analysis of carbonyl carbon of polyacrylamide was performed which has not been reported before. Finally, ^{1}H NMR via HMQC triad sequence analysis was also performed for methylene and methine groups.

EXPERIMENTAL

Materials

Acrylamide monomer was obtained from Fluka and used without purification. α,α-Azobisisobutyronitrile (AIBN) as initiator (Merck) was purified by recrystallization from methanol. Industrial ethylacetate and ethanol were used as solvents after purification by distillation.

Polymerization

Precipitated polymerization of acrylamide was conducted in 100 mL Pyrex glass reactor equipped with a condenser under nitrogen gas in water bath at 60ºC and maintained constant within ±0.1ºC of the

desired temperature. A typical polymerization batch consisted of the following materials: 10 g acrylamide, 50 mL of various mixtures of two solvents and 1% initiator based on molar ratio of monomer. The initiator was added after mixing of materials in the reactor and reaching the desirable temperature. In this way, reaction was ceased after 2 h by addition of 1% solution of hydroquinone in methanol and cooling off the reactor simultaneously. The product was filtered, dissolved in water, and reprecipitated in excess methanol and dried under vacuum at 40ºC for 24 h.

Characterization

The liquid NMR spectra were obtained on a Bruker Avance 400 MHz, Germany. Samples were concentrated in deuterium oxide about 20% (w/v) for ^{1}H NMR and 50% (w/v) for ^{13}C NMR and 2D NMR by using a 5 mm NMR tube at room temperature. ^{1}H NMR spectra were acquired using 32 k data points, spectral width 16 ppm, relaxation delay 10 s, acquisition time 1.97 s, pulse width 30º, and 4 scans. ^{13}C NMR spectra were acquired using 64 k data points, spectral width 220 ppm, relaxation delay 2 s, acquisition time 1.37 s, pulse width 90º, and 20000 scans. Nuclear overhauser effect (NOE) was suppressed by gating the decoupler sequence. Heteronuclear multiple quantum coherence (HMQC) was performed by using the standard Bruker pulse sequence with *hmqcgpqf* pulse program. The spectrum was obtained with 256 increments in the F_1 dimension and 1024 data points in the F_2 dimension, with 200 scans and relaxation delay 1.5 s.

RESULTS AND DISCUSSION

In this research, the polymer tacticity was observed by ^{13}C NMR in the incipient stage for precipitated polymers. Basically, due to higher resolution and more extensive sweep width, this technique is used in most studies. ^{13}C NMR spectra with wide magnetization field caused higher splitting which was observed for all carbons. Figure 1 shows ^{13}C NMR spectrum of polyacrylamide being synthesized in ethanol 100% as solvent in which three types of carbon are observed. Methylene carbon peak in upfield as well as that of carbonyl carbon in downfield are observed. Peaks of
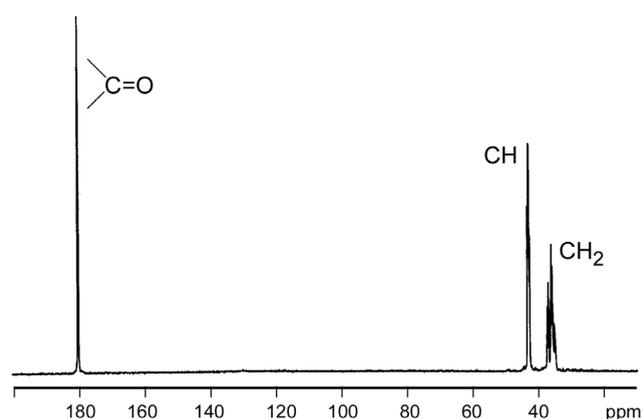

Figure 1. Proton decoupled ^{13}C NMR spectrum of polyacrylamide in deuterium oxide at room temperature.

methylene and methine carbons main chain have the highest split, and therefore their stereosequences can be studied. Assignments of sequences for methylene and methine carbons peaks were adopted as Lancaster et al. [28] which used NMR-400MHz with similar splitting for two carbons.

^{13}C NMR of Methine Carbon

The methine carbon of polyacrylamide main chain is an asymmetric carbon and is sensitive to the monomer insertion along the polymer chains. Its resonance shows different chemical shifts due to the discrepancy of the microstructure. Figure 2 shows the expansion of liquid ^{13}C NMR spectrum in deuterium oxide for methine carbon. As it is evident in Figure 2, peak of this carbon has splitted to about eight peaks in less than 1 ppm limiting of chemical shift. Therefore, in statistical analysis, it has pentad sequence distribution where right section is rich in meso sequences and the left section is rich in racemic ones.

In other words, the peaks with assignment numbers of 1 and 2 are isotactic, with 3, 4, and 5 are atactic and with 6, 7, and 8 are syndiotactic parts of the chain. The experimental data was tested for Bernoullian and 1st-order Markov statistical models of chain propagation and the results are shown in Table 1.

In statistical subject, probabilities of meso (P_m) and racemic (P_r) sequences are defined by eqns (1) and (2), respectively. The mm, mr, and rr triad sequences have isotactic, atactic, and syndiotactic parts of chain, respectively.
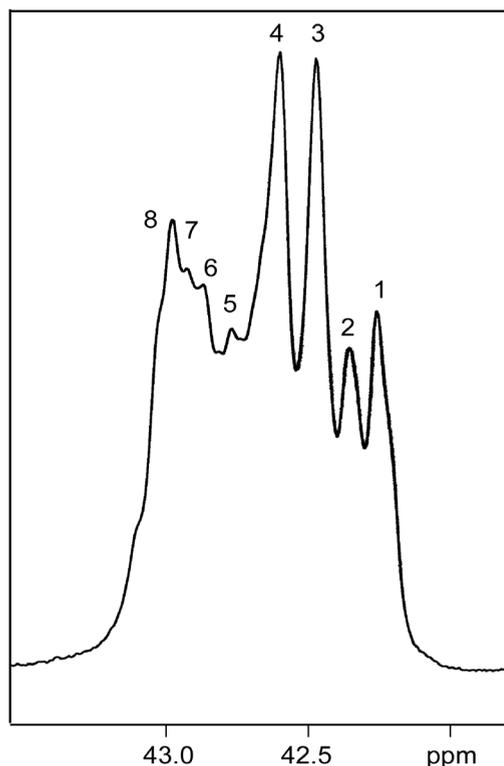
Figure 2. Expanded proton decoupled ^{13}C NMR spectrum of methine carbon in deuterium oxide at room temperature.

$$P_m = (2mm + mr) / 2 \qquad (1)$$

$$P_r = 1 - P_m = (2rr + mr) / 2 \qquad (2)$$

The relationship between pentad and triad are obtained by eqns (3)-(5) which finally enable to calculate the probability of meso (P_m).

$$mm = mmmm + mmmr + rmmr \qquad (3)$$

$$mr = mmrm + mmrr + rmrm + rmrr \qquad (4)$$

$$rr = mrrm + mrrr + rrrr \qquad (5)$$

By integrating sequences areas in Figure 2 and using eqns (1) - (5), the calculated value of P_m is equal to 0.443. Other researchers obtained approximately the same value, as well [23,28,32,33]. These results indicate that the racemic addition is almost higher than the meso one. For an ideal random condition, P_m is equal to 0.5 which shows our synthesized polyacrylamide microstructure is close to stereosequences of an ideal atactic chain [37]. Basically, in free-radical polymerization of vinylic monomers, the value of P_r is always more than the value of P_m because stereohindrance of pendant groups tend to stay away from each other and form racemic sequences. But stereoregularity of chains can be changed by increasing the polymerization temperature [39] and variation of solvent polarity [33]. In addition to P_m and P_r calculations, eqns (6) and (7) can be used to calculate the length average of meso (N_m) and racemic (N_r) sequences as follows:

$$N_m = (2mm + mr) / mr \qquad (6)$$

$$N_r = (2rr + mr) / mr \qquad (7)$$

By using eqns (3) - (7), the calculated values of N_m and N_r for polyacrylamide are 1.698 and 2.133, respectively. In theoretical estimation, length average

Table 1. Pentad sequences results of methine carbon.

Peak No.	Assignments	Chemical shift (ppm)	Observed	Bernoullian calculation	1st-order Markov calculation
1	mmmr	42.256	0.0997	0.0968	0.0887
2	rmmr+mmmm	42.350	0.0825	0.0994	0.0945
3	rmrr	42.466	0.1822	0.1531	0.1597
4	mmrr+rmrm	42.590	0.2432	0.2436	0.2579
5	mmrm	42.765	0.0966	0.0968	0.1007
6	rrrr	42.859	0.0924	0.0963	0.0834
7	mrrm	42.925	0.0530	0.0609	0.0648
8	rrrm	42.976	0.1504	0.1531	0.1466

values of meso and racemic sequences are equal to 2 for an ideal atactic structure which are approximately the same as the obtained values.

According to Bernoullian and 1st-order Markov statistical models, the formation of polymeric chains could be predicted. In 1st-order Markov polymerization, the new monomer is added to the previous sequence which governs its configuration. 1st-order Markov probability is given by eqns (8) and (9).

$$P_{m/r} = 1 - P_{m/m} = mr /(2mm + mr) \qquad (8)$$

$$P_{r/m} = 1 - P_{r/r} = mr /(2rr + mr) \qquad (9)$$

In this case, $P_{r/m}$ indicates that racemic dyad influence on the next dyad situation as a meso dyad. For example Bernoullian and 1st-order Markov statistics models for mrrmr hexad sequence, are calculated as $2P_m^2P_r^3$ and $2P_mP_{m/r}^2P_{r/r}P_{r/m}$, respectively. Therefore, according to Table 1, these results show a good agreement between observed and calculated data for pentad sequences.

^{13}C NMR of Methylene Carbon

Relative to methine carbon the methylene carbon of polyacrylamide main chain is observed at upper magnetization field. Figure 3 shows the expansion of solution ^{13}C NMR spectrum in deuterium oxide for methylene carbon. As evident in Figure 3, this carbon
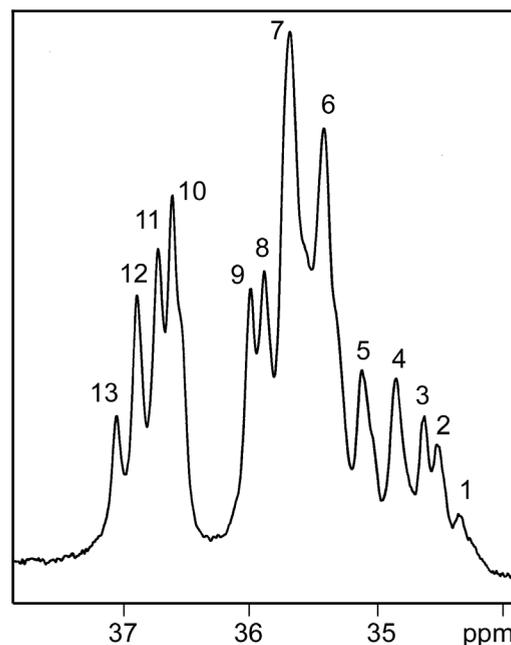

Figure 3. Expanded proton decoupled ^{13}C NMR spectrum of methylene carbon in deuterium oxide at room temperature.

has been split into about thirteen peaks in more than 3.5 ppm limiting of chemical shift. Therefore, statistically, it has hexad sequences distribution where the right section is rich in meso sequences and the left section is rich in racemic ones. The experimental data were evaluated for Bernoullian and 1st-order Markov

Table 2. Hexad sequences results of methylene carbon.

Peak No.	Assignments	Chemical shift (ppm)	Observed	Bernoullian calculation	1st-order Markov calculation
1	mmmmm	34.349	0.0140	0.0171	0.0129
2	rmmmr	34.523	0.0320	0.0270	0.0262
3	mmmmr	34.618	0.0308	0.0429	0.0366
4	mmmrm	34.851	0.0628	0.0429	0.0416
5	rmrmr+mmrmm	35.120	0.0635	0.0554	0.0630
6	mmmrr+rmmrr+mmrmr	35.404	0.1709	0.1757	0.1735
7	rmrrr+mmrrm+rmmrm+mrmm	35.680	0.2089	0.2201	0.2330
8	rmrrm	35.891	0.0649	0.0678	0.0764
9	mmrr	36.000	0.0743	0.0678	0.0606
10	mrrrr+rrmrr	36.611	0.1135	0.1279	0.1211
11	mrmrr	36.727	0.0689	0.0678	0.0678
12	rrrrr	36.895	0.0620	0.0537	0.0443
13	mrrrm	37.062	0.0335	0.0339	0.0344

Table 3. Triad sequences results of carbonyl carbon.

Peak No.	Assignments	Chemical shift (ppm)	Observed	Bernoullian calculation	1st-order Markov calculation
1	mm	180.181	0.2598	0.1963	0.1830
2	mr	180.261	0.3408	0.4935	0.5213
3	rr	180.349	0.3994	0.3102	0.2957

statistical models of chain propagation, the results are shown in Table 2.

According to measured data and relations among dyad, tetrad, and hexad sequences, like the methine carbon, the probability of meso and racemic sequences can be determined [37]. Since there are some overlaps, the determination of hexad sequences of methylene carbon, i.e., P_m is complicated.

^{13}C NMR of Carbonyl Carbon

The carbonyl carbon of polyacrylamide side chain is observed at the highest magnetization field in comparison with the other carbons, while splitting of its peak is limited. Figure 4 shows the expansion of liquid ^{13}C NMR spectrum of carbonyl carbon in deuterium oxide. According to Figure 4, this carbon is split to about three peaks in less than 1 ppm limiting of chemical shift. Therefore, statistically, it has triad sequences distribution where right section is rich in meso sequences and the left part is rich in racemic

ones. In other words, peak assignment numbers of 1, 2, and 3 are isotactic, atactic and syndiotactic sequences, respectively. The experimental data was tested for Bernoullian and 1st-order Markov statistical models of chain propagation, the results are shown in Table 3.

By integrating sequences area in Figure 4 and using eqn (1), calculated value of P_m is equal to 0.430 which indicates the calculation is approximately the same as the methine carbon calculation. Therefore, P_m obtaining via calculation of the carbonyl carbon is considered a simple and rapid way, but, due to better splitting of the methine carbon, its P_m calculation is more reliable. By using standard deviation between two models and experimental data, adjustment of Bernoullian and 1st-order Markov models can be comprised for all the carbons as it is shown in Table 4.

According to Table 4, for all carbons, the standard deviation results of Bernoullian statistics model are fitted better than 1st-order Markov statistics model. Thus, Bernoullian statistics model can predict the formation of monomers in polymer propagation more effectively. Lancaster et al. [28] have only conformed to Bernoullian statistical model and obtained the satisfactory results for acrylamide solution polymerization method.

Figure 4. Expanded proton decoupled ^{13}C NMR spectrum of carbonyl carbon in deuterium oxide at room temperature.

Table 4. Standard deviation results between observed and calculated data.

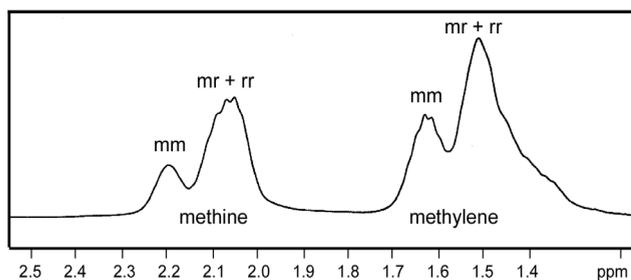| Type of Carbon	Standard deviation ($\Sigma <d>^2/n$)	
	Bernoullian	1st-order Markov
Methine	1.53×10^{-4}	1.55×10^{-4}
Methylene	8.69×10^{-5}	1.38×10^{-4}
Carbonyl	1.18×10^{-2}	1.64×10^{-2}

Figure 5. Expanded ¹H NMR spectrum of aliphatic region from polyacrylamide in deuterium oxide at room temperature.

Tacticity Investigation by ¹H NMR via 2D NMR

Figure 5 shows the aliphatic expansion of solution ¹H NMR spectrum in deuterium oxide for methine and methylene protons. As it is demonstrated in Figure 5, methylene and methine protons would be observed in 1.26-1.73 ppm and 1.95-2.30 ppm regions, respectively and each proton's peak has been split into about two peaks. 2D NMR and relations between heterogeneous nuclei can be used for the assignment of each proton peak in ¹H NMR.

HMQC is the useful technique for direct correlation between protons and carbons of methylene and methine groups. Utilizing proton detection which has very high sensitivity can show results quicker than a
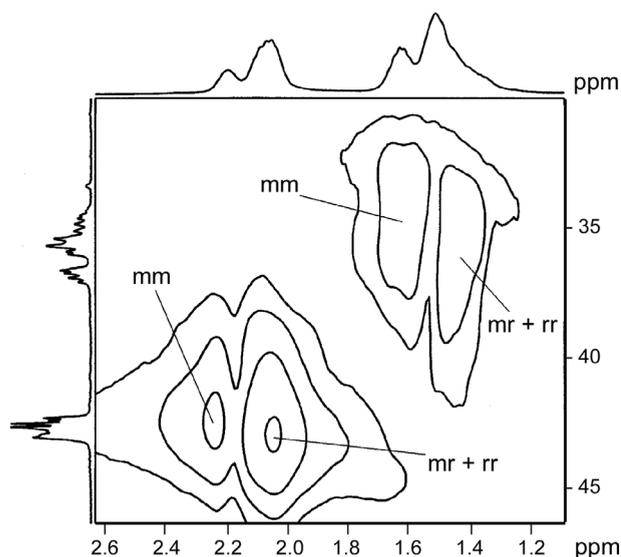
1D carbon spectrum. The correlations can be used to map known proton assignments onto their direct attached carbons. HMQC spectrum can also be helpful in the assignment of the proton spectrum by dispersing the proton resonances along the ¹³C dimension and reducing its multiplet overlaps.

Figure 6 shows the HMQC spectrum of polyacrylamide aliphatic regions and their triad sequences. As it is seen in Figure 6, isotactic placements are observed separately, while syndiotactic and atactic placements are overlapped together in the spectrum of methylene and methine groups. Thus, in ¹H NMR spectrum of polyacrylamide, the low and high intensities of peaks for both methylene and methine protons are attributed to isotactic and overlapping of syndiotactic and atactic placements, respectively. Isotactic placement value can be calculated by using the integration of areas for both methylene and methine protons (mm = 0.21 and mr + rr = 0.79).

Effect of Solvents with Various Molar Ratio Contents on Tacticity

Stereoregularity experiments of free-radical polymerization of acrylamide were applied in heterogeneous systems by using various molar ratios of ethanol and ethylacetate as solvents. Figure 7 shows the effect of various molar ratios of ethanol and ethylacetate versus probability of meso sequence. According to Figure 7, results of meso sequence in various ratios of two solvents are equal. But, the highest content of meso sequence was obtained when
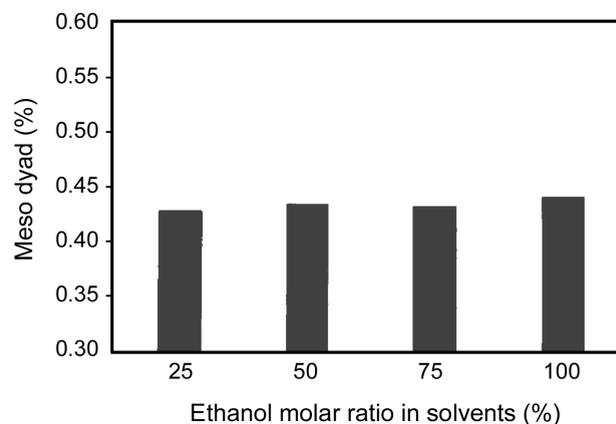

Figure 6. Expanded 2D HMQC NMR spectrum of aliphatic region from polyacrylamide in deuterium oxide at room temperature.

Figure 7. Effects of the ratios of two solvents on the probability of meso structure.

ethanol was only used as solvent. Habaue et al. [33] showed that the polar solvents such as methanol are more efficient than other solvents to change stereoregularity of polymer chains in free-radical polymerization. They have concluded that in solution polymerization of (metha)acrylamide and its derivatives in methanol, isotactic part of poly-acrylamide chains increased slightly and shifted to ideal atactic. Therefore, according to Figure 7, polarity decreases in mixed solvents cause slight decrease in isotactic part of polyacrylamide. In fact, polar solvent might coordinate with the pendant groups of the macroradical terminal and new monomer and consequently force them into the meso configuration during propagation step, leading to formation of isotactic segment in polymerization.

CONCLUSION

Free-radical precipitated polymerization of acry-lamide was carried out in various molar ratios of ethanol and ethylacetate as solvents. Assignment of all stereosequences was performed on methine carbon at pentad, methylene carbon at hexad, and carbonyl carbon at triad sequences level by using ^{13}C NMR spectroscopy. Acceptable compatibility for these results indicated that acrylamide monomer has slightly more tendency to add by racemic configuration to its growing free-radical precipitated polymerized chains and polymer microstructure is near to an ideal atactic structure. The standard deviation results showed that, Bernoullian propagation is fitted pretty well by experimental results. Changing the molar ratios of ethanol and ethylacetate as solvents did not affect the stereoregularity of polyacrylamide, seriously. ^{1}H NMR via HMQC triad sequence analysis was also performed for methylene and methine protons and it was shown that only the calculation of isotactic place-ment could be determined by ^{1}H NMR.

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