The Research of Preparation of Polyvinyl Acetate with Lower Polydispersity Index

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Received 21 June 2007; accepted 9 January 2008
DOI 10.1002/app.28192
Published online 15 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, the way of preparing polyvinyl acetate (PVAc) with lower polydispersity index (PDI) was studied. By adding small amount of monomer with polar group, such as acrylic acid (AA), α-methacrylic acid (MAA), or acrylamide (AM), as modulation monomer, the polymerization was carried out at 65°C with a mechanical agitator using AIBN as initiator under N_2 atmosphere. Effects of the mol ratio of modulation monomer/VAc and structure of the modulation monomer on the polymerization conversion, the molecular weight and molecular weight distribution of the obtained polymers were investigated through ^{1}H NMR, gravity method, and gel permeation chromatography. The results show that by adding modulation monomer into the reactive system the PVAc with lower PDI could be got. With the increase of the modulation monomer amount, the conversion and the molecular weight decrease, and the PDI of the obtained polymer is lower. When the mol ratio of AA/VAc is 3 : 100, the PDI of the obtained polymer is 1.84. When the mol ratio of AM/VAc is 1 : 100, the PDI of the obtained polymer is 1.68, which is narrower than that without AM. All researches we have done laid a foundation for further study. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1122–1128, 2008

Key words: vinyl acetate (VAc); acrylic acid; acrylamide; copolymerization; polydispersity index; block copolymers; copolymerization; NMR; structure

INTRODUCTION

Vinyl acetate is an important monomer and its polymers are used in applications ranging from adhesives, paints, concrete additives to pharmaceuticals.[1] Especially the use of polyvinyl acetate (PVAc) within pharmaceutical context as a precursor to polyvinyl alcohol (PVA) makes the preparation of polyvinyl acetate with lower PDI extremely desirable. It is valuable to find out one way to prepare PVAc with lower PDI. Vinyl acetate (VAc) is a typical example that cannot easily be polymerized, since its free radical is easy to chains transfer or radical combination for its higher energy. It is difficult to prepare PVAc with lower PDI.

In general, there are four main means to get lower PDI by radical polymerization of some vinyl monomers, i.e., atom transfer radical polymerization (ATRP),[2,3] nitroxide mediated polymerization (NMP),[4] reversible addition fragmentation chain transfer polymerization (RAFT)[5,6] and degenerative transfer polymerization (DT). There has only limited success for a controlled polymerization of VAc using the RAFT process and the used reagent is poisonous and not easy to be prepared.

According to characteristics of radical polymerization of VAc, factors such as radical concentration and reaction temperature etc. should be controlled to avoid radical transferring and terminating. In this study, three methods are introduced to prepare PVAc with lower PDI. The first is to process reverse atom transfer radical polymerization (RATRP), the second is to decrease the reaction temperature by using oxidant–reductant initiating system and the third is to copolymerize VAc with some vinyl polar monomers.

EXPERIMENTAL

Materials

Vinyl acetate (analytic reagent grade, A.R), acrylic acid (A.R), methanol (A.R) and α-methacrylic acid (MAA) (A.R) were obtained from Tianjin Bodi Chemical Reagent Factory (Tianjin City, China) without further treatment. Ammonium iron(II) sulfate hexhydrate ($(NH_4)_2Fe(SO_4)_2$) (A.R) was obtained from Tianjin Nankai Chemical Reagent Factory (Tianjin City, China) without further treatment. Copper(II) chloride dehydrate($CuCl_2$) (A.R), AM (A.R), ammonium persulfate($(NH_4)S_2O_8$) (A.R), sodium pyrosulfite ($Na_2S_2O_5$) (A.R) all came from Chengdu Kelong Chemical Reagent Factory (Chengdu City,

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20374036.

China) without further treatment. AIBN (A.R) was obtained from Beijing Chemical Reagent Factory (Beijing City, China). 2-2′-bipyridine (bpy) (A.R) came from Beijing Shiying Chemical Reagent Factory (Beijing City, China).

The preparation of PVAc by Ratrp

Under the magnetic agitation, VAc, $CuCl_2$, bpy, AIBN, and methanol were charged into a reactor successively and mixed completely. Then the reactor was degassed under vacuum and charged with N_2 (three times). The polymerization was carried out at 65°C for 4 h, and during the process the sample was quickly taken out into a 25-mL weighing bottle every 60 min. Finally, the obtained PVAc was dried at 65°C for 36 h.

The preparation of PVAc by $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$ oxidant–reductant

Under the magnetic agitation, VAc, $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$ and methanol were charged into a reactor successively, and mixed completely. Then the reactor was degassed under vacuum and charged with N_2 (three times). The polymerization was carried out at 20°C for 3 h, and during the process the sample was quickly taken out into a 25-mL weighing bottle every 60 min. Finally, the obtained PVAc was dried at 65°C for 36 h.

The preparation of PVAc by copolymerization of VAc with vinyl polar monomer

VAc, AIBN, and methanol were charged into a reactor successively and mixed completely, where AIBN-was first dissolved into VAc and then charged into a reactor. Then the reactor was degassed under vacuum and charged with N_2 (three times). Vinyl polar monomer such as AA, MAA, and AM was dripped into the reactor. The polymerization was carried out at 65°C for 3 h, and during the process the sample was quickly taken out into a 25-mL weighing bottle every 60 min. Finally, the obtained polymer was dried at 65°C for 36 h.

Characterization

The conversion (C%) of monomer was measured by gravity method and calculated by the following equation:

$$C\% = \frac{(W_3 - W_1) - (W_2 - W_1) \times N}{(W_2 - W_1) \times M} \times 100\%$$

where, W_1 is the weight of empty weighing bottle, W_2 is the weight of weighing bottle in which the sample was added, W_3 is the weight of weighing bottle with dried sample, M is the weight percent of monomer to the total weight of reactant, N is the weight percent of such substances as bpy and $CuCl_2$ whose weight did not change after reaction.

The molecular weight and the polydispersity index (PDI) of the obtained polymer were measured on a Waters 150C gel permeation chromatography (GPC) equipped with styragel columns and THF as solvent at 25°C.

1H NMR spectra were recorded on a JNM-EXC 400 Hz nuclear magnetic resonance spectrometer(NMR). Chloroform was used as solvent.

Differential scanning calorimeter of Dupond 2100 Instrument was used to determine the glass transition temperature of the obtained polymer. Samples were heated from −50 to 150°C at 10°C min^{-1} in N_2.

RESULTS AND DISCUSSION

Preparation of PVAc by Ratrp

RATRP is a developing way of ATRP, and is easier to get polymer with lower PDI. In the previous work, we had succeeded in polymerization of styrene by RATRP in the microemulsion.[7] In the present study, we try to getI PVAc with lower PD by this means. The ''living'' character by the way of adding AIBN/$CuCl_2$/bpy in the solution is introduced. There maybe set up a reversible balance between a conventional radical initiator (AIBN) and a catalyst composing $CuCl_2$ and bpy. In the reaction, the mol ratio of AIBN/$CuCl_2$/bpy was 1 : 1 : 2 or 1 : 1 : 3, VAc/methanol was 4 : 1. The reaction can not process well and there was no polymer in the reactor.

Preparation of PVAc by oxidant–reductant initiator system

The oxidant–reductant initiator can make the monomer polymerize at lower temperature, which would be benefit in controlling the chain transfer during polymerization of VAc and hence to get PVAc with lower PDI. The oxidant–reductant used here is the system of $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$ and the reaction temperature is 20°C. To understanding weather the PVAc with lower PDI can be prepared by using oxidant–reductant, the result of conversional polymerization of VAc is introduced. Figure 1 is the GPC spectrum of polymer initiating by AIBN and Figure 2 is the GPC spectrum of polymer initiating by oxidant–reductant system with 25 : 200 : 1 mol ratio of $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$. The molecular weight and PDI obtained from Figures 1 and 2 are all showed at Table I. Table I also shows the relationship between conversion and mol ratio of $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$.

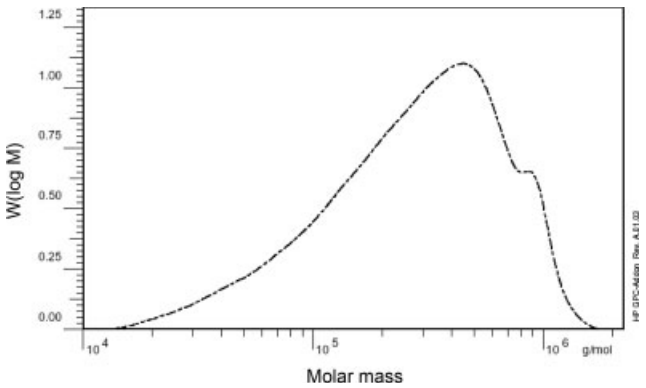

Figure 1 GPC spectrum of polymer initiating by AIBN (AIBN/VAc = 0.05 : 100).

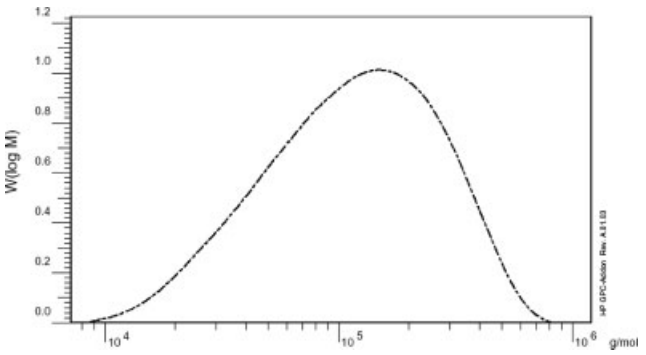

Figure 2 GPC spectrum of polymer initiating by oxidant–reductant system $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$ (mol ratio) = 25 : 200 : 1).

It can be seen from Table I that the conversion and molecular weight are all decrease with the increase of $Na_2S_2O_5$. The conversion decreases from 35.6 to 10.2% when the mol ratio of $((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$ changes from 25 : 100 : 1 to 25 : 400 : 1. The molecular weight of the obtained polymer decreases from 7.71×10^4 to 6.09×10^4. For all the systems, the PDI of the obtained polymer is larger than 2.0, though it is lower than PDI (2.2) of the polymer prepared by conventional polymerization, indicating a broader molecular weight distribution. The initiator system of oxidant–reductant can make the reaction temperature decrease but the PDI of the obtained polymer is not low enough as we expected. It is necessary to find out another way to get PVAc with lower PDI.

Preparation of PVAc by introducing vinyl polar monomer

According to characteristics of polymerization of VAc, chain transfer and chain termination occur easily due to activity of the corresponding radicals, leading to a broader molecular weight distribution. If the properties of the radicals could be changed, i.e., the stability of the radicals be enhanced, the polymerization would be improved. In the next section, some vinyl polar monomers such as AA, MAA, and AM will be introduced to modulate the polymerization and hence to get polymer with lower PDI. There are domino effects of conjugate between ethylene and functional groups in these monomers, so the free radicals of these monomers could be improved.

Preparation of PVAc by introducing AA

In the copolymerization between VAc and AA, the reaction parameter of VAc is 0.018 and the reaction parameter of AA is 20.6 at 65°C,[8] indicating that VAc prefers to copolymerize with AA but AA prefers to copolymerize with himself. A polymer with lower PDI may be got by this way when the reaction conversion is not very high.

In the study, effect of AIBN on the polymerization is first investigated and the result is showed in Figure 3. It can be seen from Figure 3 that AIBN has effect on the polymerization. With the increase of the amount of AIBN based on VAc, the polymerization rate and the final conversion increase. The curve with the AIBN content is more than 0.1% differences between the other two curves. Second, effect of the mol ratio of AA to VAc on the preparation of PVAc is studied. Figure 4 is the GPC spectra of polymers prepared by adding AA. The molecular weight and PDI got from Figure 4, as well as conversion are all listed at Table II.

From Table II, it can be seen that the conversions of all system decrease with the increase of AA, and

TABLE I
Results of Preparation of PVAc by Oxidant–Reductant Initiating Systems

$((NH_4)S_2O_8)/Na_2S_2O_5/(NH_4)_2Fe(SO_4)_2$ (mol ratio)	Reaction temperature (°C)	Reaction time (h)	Conversion (%)	$M_n \times 10^{-4}$	PDI
0	65	3	43.2	16.99	2.2
25 : 100 : 1	20	4	35.6	7.71	2.12
25 : 200 : 1	20	4	28.1	6.69	2.01
25 : 400 : 1	20	4	10.2	6.09	2.3

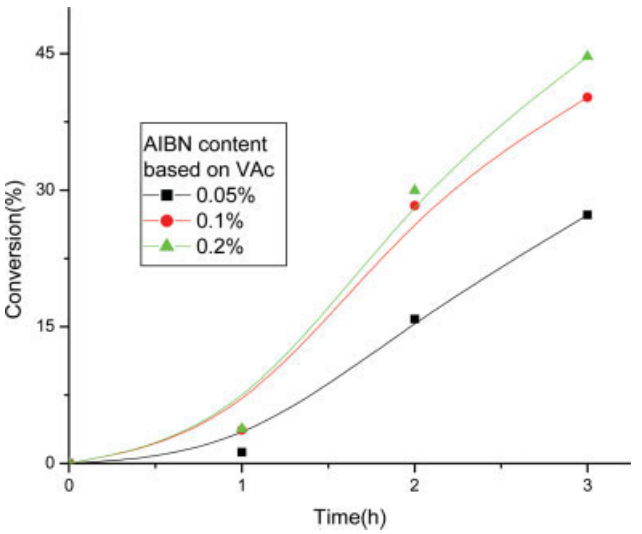

Figure 3 Conversion versus time with different AIBN content based on VAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the conversion is about 28.7% when the mol ratio of AA to VAc is 5% after reacting 3 h. The molecular weight of the produced polymer changes little with increase of AA. And when mol ratio of AA to VAc is 3%, the PDI of the produced polymer is 1.84. From Table II, it can also be seen that the PDI of PVAc decreases from 1.84 to 1.83 when the react temperature decreases from 65 to 50°C, and the conversion decreases more with decreasing reaction temperature. When the reaction temperature is lower than 30°C the reaction cannot process well.

Figure 5 shows the relationship between convention and the reaction time with different mol ratio of AA/VAc. It can be seen that the change trend of the increase of convention with the time for all systems are same. With the increase of time, the convention increases slowly at first and then fast and comes to a high point. There are also some differences between every curve, i.e., when the amount of AA in the reaction is less the extent of increase of convention is faster.

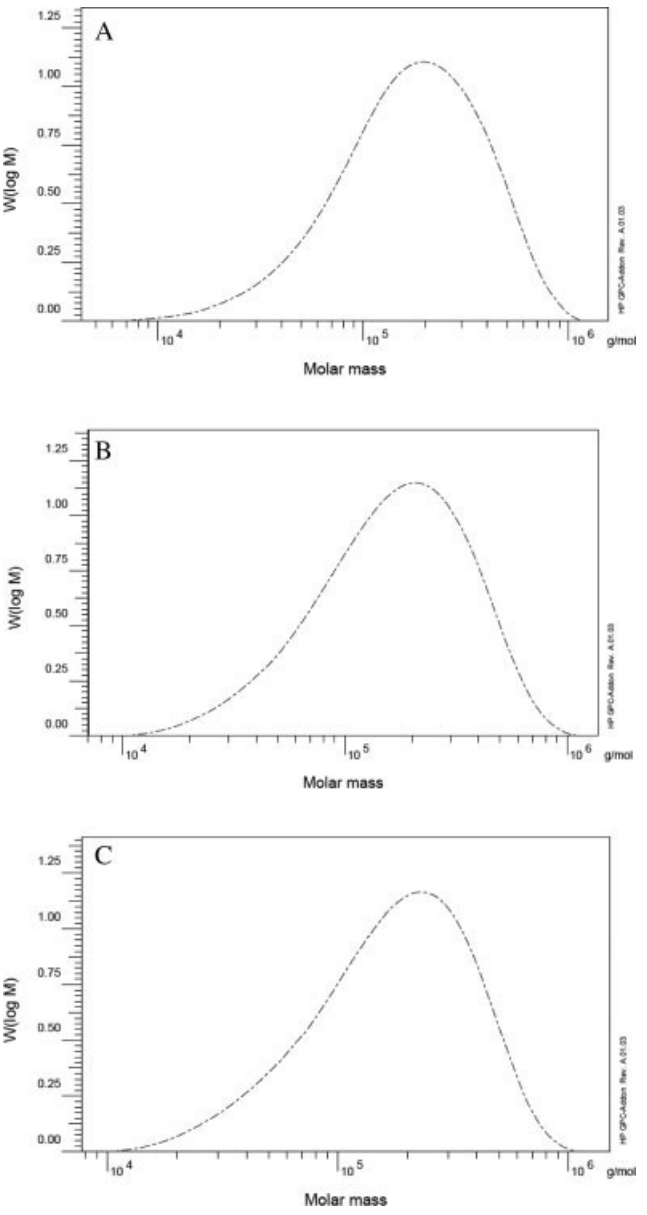

Figure 4 GPC spectra of polymer prepared by different mol ratio of AA/VAc. (A) AA/VAc = 1 : 100. (B) AA/VAc = 3 : 100. (C) AA/VAc = 5 : 100.

TABLE II
Results of Preparation of PVAc by Introducing AA

AA/VAc (mass%)	Reaction temperature (°C)	Reaction time (h)	Conversion (%)	$M_n \times 10^{-4}$	PDI
0	65	3	43.2	16.99	2.2
0.5	65	3	41.3	11.51	2.12
1	65	3	39.5	11.3	1.97
3	65	3	34.3	11.47	1.84
5	65	3	28.7	11.76	1.87
3	50	3	29.2	11.32	1.83
3	30	3	–	–	–

Note that ''–'' expresses the result not existed in the system.

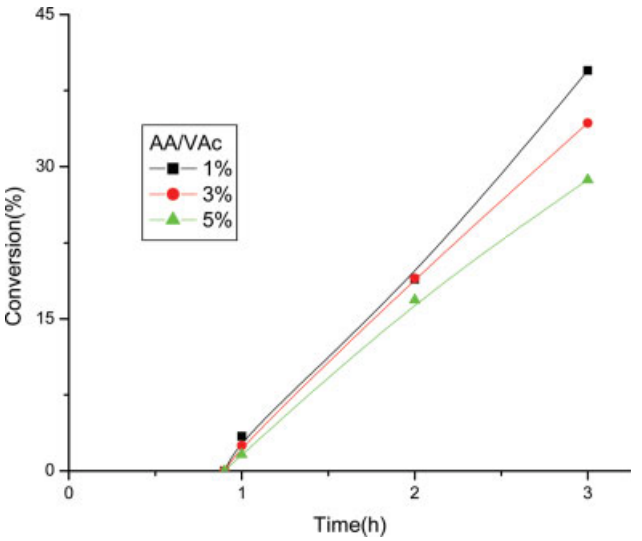

Figure 5 Conversion versus time with different mol ratio of AA/VAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

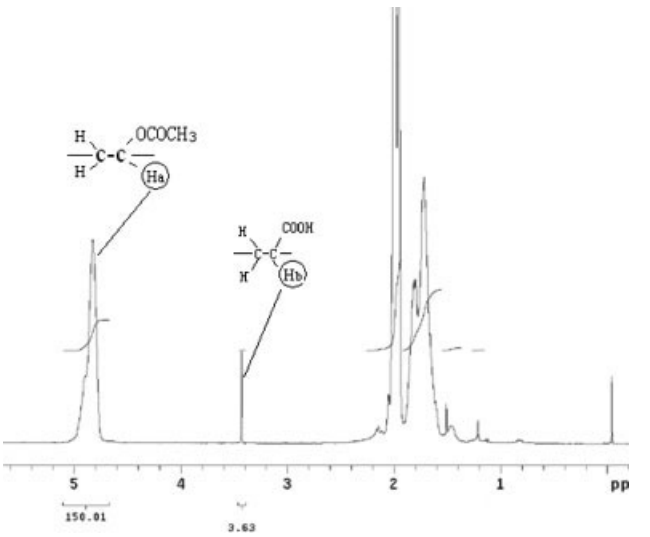

Figure 7 ^{1}H NMR spectrum of polymer prepared by copolymerization of VAc with AA. (AA/VAc (mol ratio) = 3 : 100).

From the above results, it can be drown that when the mol ratio of AA/VAc is 3 : 100, AIBN/VAc is 0.1% and the reaction temperature is 65°C, a polymer with lower PDI (1.84) ,higher molecular weight (11.47×10^4), and higher monomer conversion (34.3%) can be obtained, which is very important for preparation of PVAc with lower PDI.

Figure 6 shows DSC curve of polymer prepared by introducing AA and the mol ratio of AA/VAc in react system was 3 : 100. It can be seen that the glass transition temperature of the obtained polymer is 75.2°C, much higher than that of pure PVAc (28°C) and lower than that of polyacrylicacid (106°C), indicating that there might only one substance exist in the product, which is the copolymer of VAc with a little AA.

Figure 7 is ^{1}H NMR spectrum of polymer prepared by introducing AA. As we know that the area of wave crest of H means the proportion of this special H in the polymer. Figure 7 shows that the mol ratio of the single H in hypomethyl of PAA to PVAc is 3.63 : 150.01, about 2.42%. For the mol weight of () is 72 and () is 86, so the mass ratio of PAA in the obtained polymer is only (2.42 × 72/86) % = 2.03%, and the properties of PVAc would not be affected.

Preparation of PVAc by introducing α-methacrylic acid

It has been done to add a little MAA into the reaction system to get PVAc with lower PDI. In the reaction system, the mol ratio of MAA to VAc is from 0 to 3%. Figure 8 is the GPC spectrum of polymer prepared by introducing MAA, and the corresponding date, and the conversions are all listed in Table III.

It can be seen from Table III, that with increase of MAA the conversion decrease, when the mol ratio of MAA to VAc is 2% the conversion is about 10.3%,

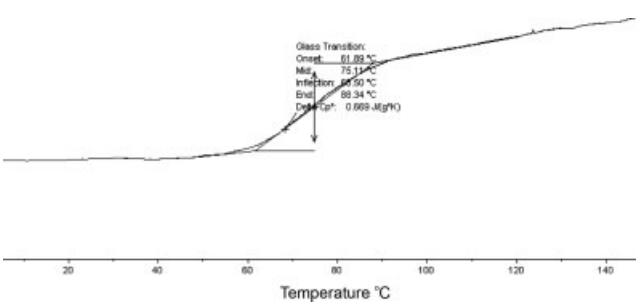

Figure 6 DSC spectrum of polymer prepared by introducing AA. (AA/VAc (mol ratio) = 3 : 100).

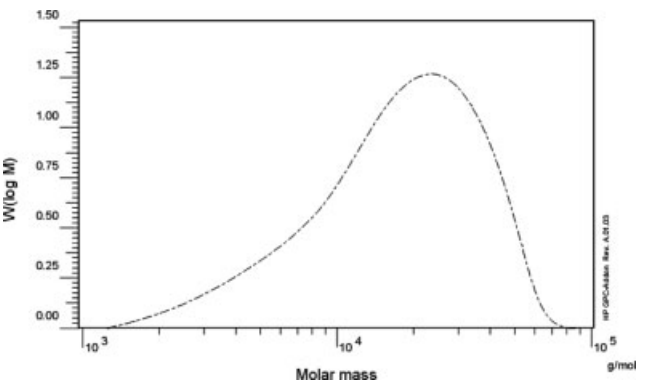

Figure 8 GPC spectrum of polymer prepared by introducing MAA (MAA/VAc = 1 : 100).

TABLE III
Results of Preparation of PVAc by Introducing MAA

MAA/VAc (mass%)	Reaction time (h)	Conversion (%)	$M_n \times 10^{-4}$	PDI
0	3	43.2	16.99	2.2
0.5	3	31.4	2.56	1.80
1	3	21.2	1.19	1.76
2	3	10.3	1.12	1.75

indicating that more MAA would take low conversion. Not only molecular weight but also PDI of the obtained polymer decreases with increase of MAA/VAc ratio, and when mol ratio of MAA to VAc is 1% the PDI of PVAc is 1.76.

Figure 9 shows the relationship between conventions and time. It can be seen from Figure 9 that the convention of three systems have the same increasing trend with the increase of time, and the corresponding convention in system with 0.5% mol ratio of MAA/VAc is higher than that of other two systems.

Preparation of PVAc by introducing acrylamide

It also has been done to add a little AM into the reaction system to get PVAc with lower PDI. The mol ratio of AM to VAc is from 0.5 to 2%. Figure 10 is the GPC spectrum of polymer prepared by adding AM, and the corresponding data, and the conversion are listed in Table IV.

It can be seen from Table IV that the conversion, the molecular weight, and PDI of obtained polymer are all decrease with increasing AM in the reaction system, but the conversion decreases slowly and the PDI decreases fastly in special range. When the mol ratio of AM/VAc is 1 : 100, molecular weight and PDI of obtained polymer are 9.37 $\times$ 10^4 and 1.68, respectively, and the conversion reaches 38.76%. Results of Figure 11 indicate that when mol ratio of AA/VAc is 1% the conversion is highest and the PDI is lower.

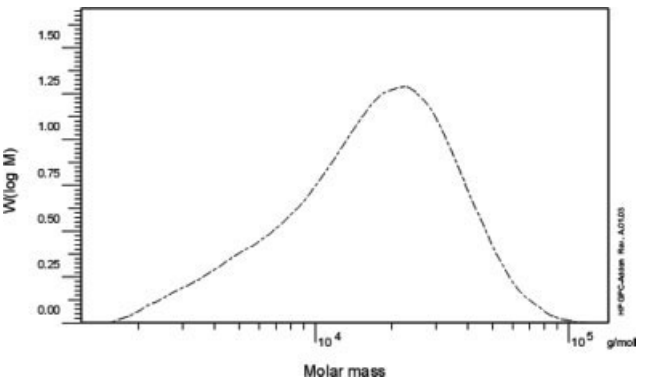

Figure 10 GPC spectrum of polymer prepared by introducing AM. (AM/VAc = 1 : 100).

TABLE IV
Results of Preparation of PVAc by Introducing AM

AM/VAc (mass%)	Reaction time (h)	Conversion (%)	$M_n \times 10^{-4}$	PDI
0	3	43.2	16.99	2.2
0.5	3	42.57	10.21	2.01
1	3	38.76	9.37	1.68
3	3	10.58	–	–

Note that ''–'' expresses the result not existed in the system.

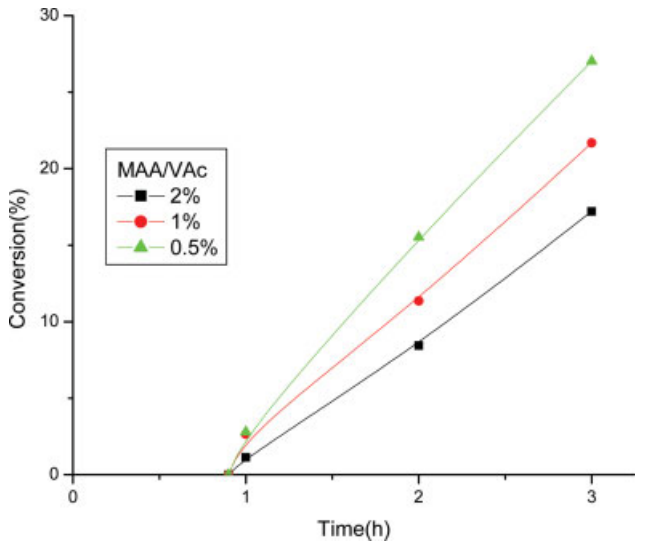

Figure 9 Conversion versus time with different mol ratio of MAA/VAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

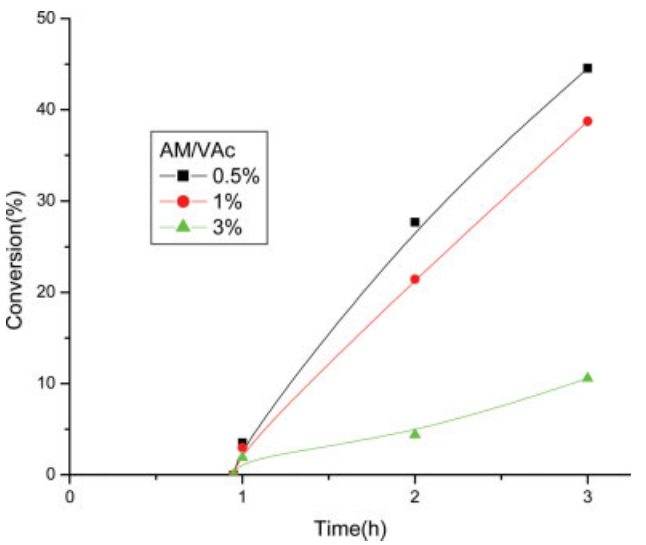

Figure 11 Conversion versus time with different mol ratio of AM/VAc. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

1. It is difficulty to obtain PVAc with lower PDI by Ratrp.
2. The introduction of oxidant–reductant initiator system can decrease the reaction temperature and hence decrease PDI of PVAc, but the PDI is not as low as 2.0.
3. The introduction of a little AA in the system can get PVAc with lower PDI. When the mol ratio of AA/VAc is 3 : 100, the conversion can reach 34.3%, and the molecular weight and PDI are 11.47×10^4 and 1.84, respectively, and AA unit content in the polymer is only about 4.6%, which would not affect the properties of the PVAc.
4. The introduction of a little MAA or AM in the system can get PVAc with lower PDI. The PDI of obtained PVAc is 1.76 when the mol ratio of MAA/VAc is 1 : 100, but the conversion (21.2%) is too low. When the mol ratio of AM/VAc is 1 : 100, the PDI of obtained PVAc is 1.68, molecular weight is 9.37×10^4, and the conversion is 38.76%.

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