Lightly Branched Poly(vinyl alcohol) for Fluid Loss Additive

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ABSTRACT: One kind of branched Poly(vinyl alcohol) has been synthesized via common radical copolymerization of vinyl acetate in methanol by adding a bifunctional monomer Allyl methacrylate (AMA) followed by saponification. The comonomer AMA has two reactive double bonds that can provide the branching points to macromolecule chain structure. With these reactive points, the copolymer with long chain branches can be obtained. The long chain branches bring the copolymer higher viscosity by the entanglement of them between macromolecules and strong hydrogen bonding between long chain branches. The viscosity of the water solutions increased with the amount of the comonomers' addition increased. The branched PVA has good water maintenance properties at relatively high temperature. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4608–4612, 2013

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a kind of water soluble polymer, which is generally used in many fields of human life, such as PVA fiber, weave pulp, coating, adhesives, emulsifier, membrane for package, drug slow-release system, and so on. PVA cannot be prepared by direct polymerization owing to tautomerism of vinyl alcohol monomer.[1,2] Thus, PVA is obtained by the saponification of a poly(vinyl ester), such as poly(vinyl acetate) (PVAc), poly(vinyl pivalate).[3,4] Because of the water soluble property, PVA can be used as the fluid loss additive in drilling fluid that is very important in oil exploitation. PVA has a great amount of hydroxyl that can react with borax forming cross-linked networks to keep water and mud for maintaining the drilling fluid in normal viscosity.[5,6] But the common PVA product that is the linear macromolecule and has low ability to keep the water in drilling fluid for that the linear PVA just react with borax into low degree of cross-linked network because of the low degree of reaction between the certain number of reactive groups. And the cross-linked networks are not so stable for the shearing force that is from the flow of the drilling fluid.[7–9] That will make the amount of effective networks decreased. Then the ability to keep the water will be weakened. As a consequence, the water from the drilling fluid will be permeated into the stratum. That makes the drilling fluid more thick and become difficult to flow.[10,11] That will result in a lower well or wasting greater energy to build a deep enough well. Because of that, finding a better polymer as fluid loss additive in drilling fluid is becoming more important for exploiting oil. That is the main reason why we design to develop a branching type water soluble PVA product for keeping water better as fluid loss additive in the drilling fluid.

Many ways have been discovered to produce branched polymer, such as single monomer methodology (SMM), double-monomer methodology.[12,13] There are at least four components for SMM: (1) poly-condensation of ABn monomers; (2) self-condensing vinyl polymerization; (3) self-condensing ring-opening polymerization; and (4) proton-transfer polymerization. Obviously, condensation is the essence of this kind of method to synthesize branched polymer. Differently, SMM is meaning that direct polymerization of two suitable monomers or a monomer pair gives rise to branched polymers. For example, the polymerization of A_2 and B_n ($n > 2$) monomers, is well known. The way taken by us to produce the branched PVA is seen as SMM. And the branched polymer synthesized by the polymerization is difficult to control the structure and molecular weight.[14]

In general, there are four polymerization methods of VAc including bulk, solution, emulsion, and suspension—are known. The solution polymerization method has advantages of easy control of polymerization exotherm and simpler polymerization process than other methods of polymerization.[15] It also can get pure polymer by removing the volatile solvent easily, thus we take it as the appropriate way to get the branched PVAc, then followed by saponification to obtain the branched PVA. Without the comonomer, the branches can be formed by chain transfer reaction.[16,17] Branching of vinyl acetate occurs by three reactions: chain transfer to monomer (which gives a polymer
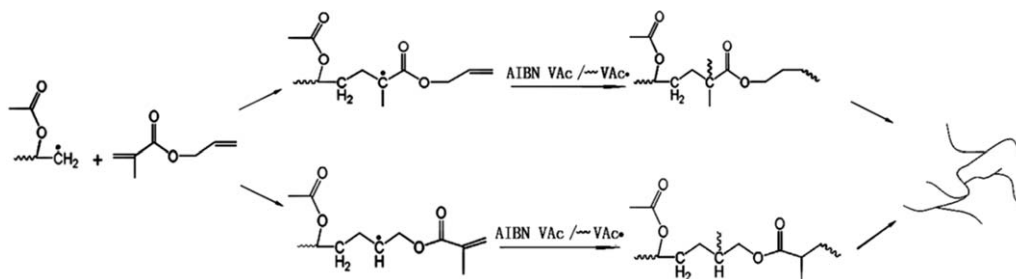
Scheme 1. The synthesis of branched polyvinyl alcohol.

molecule with a terminal double bond), chain transfer to polymer (which polymerizes with VAc to give a trifunctional branch point in the polymer molecule), and the terminal double bond polymerization in which an entire polymer molecule adds to a growing polymeric radical.[18–22] That means the perfect linear polymer here does not exist. And this kind of degree of branching can be ignored compared with these results from copolymerization. Because of that the rate of propagation is much faster than the rate of chain transfer in vinyl acetate polymerization. In PVAc polymerization the k_p (rate of propagation) >> k_{tr} (rate of chain transfer). This leads to a low degree of branching. In this paper, the method for synthesis of branched PVA and some properties of this polymer will be introduced. Scheme 1 shows the synthesis route of branched PVA with comonomer AMA.

EXPERIMENTAL

Materials

VAc (Sinopec Sichuan Vinylon Works, 99.0%) was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, and then distilled under reduced pressure of nitrogen. Methanol (Sichuan Vinylon Works, 99.9%) was used without further purification. Azobisisobutyronitrile (AIBN) (Tianjing Kermel Chemical Reagents, 99.0%) was recrystallized in methanol. Allyl methacrylate (AMA) (Acros, 99.0%) was used without further purification.

Polymerization

Forty grams of VAc, 10 g of methanol were mixed in a 250-mL three-necked round bottom flask and flushed with dry nitrogen. 10 mg of AIBN was added into the solution. Stirring the solution with teflon agitator arm to make the homogeneous solution. The reaction temperature was set at 67°C and the reaction time was 4.5 h. After the completion of polymerization, the unreacted monomers were distilled out. Conversion was calculated by measuring the weight of the polymer. Different amount of AMA were introduced into the polymerization system to obtain different branched points in polymer matrix, the amount of AMA were 2, 4, 6, and 8 mg, respectively. The products were dried under vacuum at 50°C for 24 h. The conversions of VAc are around 45%. The polymerization conditions are given in Table I.

To a solution of 8 g of PVAc in 100 mL of methanol, 2.5 mL of 5% NaOH methanol solution was added, and the mixture was stirred for 0.5 h at 45°C to yield PVA. The PVA produced was

filtered and washed well with methanol, then was dried under vacuum at 60°C for 24 h.

Characterization

The molecular weight of PVAc and the molecular distribution were determined by gel permeation chromatography (GPC) (Water 1525). Using polystyrene standards samples with tetrahydrofuran as the eluent.

The structures of branched polyvinyl alcohol were determined by ^{1}H NMR (Bruker AV II-400 MHz). The measuring conditions were as follows: solvent, d_6-DMSO; internal standard, tetramethylsilane; test temperature, 25°C.

Changes in the degree of crystallinity of the samples were characterized by Differential Scanning Calorimetry (DSC). The model is Netzsch DSC 204.

Changes in the shear viscosity of the solutions were observed by using a rheometer (Brookfield DV-III ULTRA) at a range of shear rates from 10 to 120 s^{-1}. The concentration of the aqueous solution is 4 wt %.

Static Filtration tests were taken to evaluate the sample's ability to keep water. High temperature and high pressure filtration apparatus (GGSD71) was purchased from Qingdao senxin. The steps of the test include: (1) making the cement slurry, (2) thickening the cement slurry with fluid loss additive that was made from PVA and borax at 90°C under 15 MP for 1 h, and (3) collecting the filtered water for 30 min and measuring the volume. The thickening cement slurry consists of cement slurry, PVA and borax. The percentage of cement slurry, PVA and borax are 97.98, 1.96, and 0.06 wt %. Sample 1# (linear PVA) and 5# (branched PVA) will be tested by Static Filtration tests to evaluate their abilities of keeping water as the fluid loss additive in drilling oil well. The testing temperatures were chosen as

Table I. Parameters for Solution Polymerization

	VAc (g)	Methanol (g)	AIBN (mg)	AMA (mg)	Conversion
1#	40.0	10.0	10.0	0.0	45.7%
2#	40.0	10.0	10.0	2.0	44.8%
3#	40.0	10.0	10.0	4.0	45.3%
4#	40.0	10.0	10.0	6.0	45.1%
5#	40.0	10.0	10.0	8.0	45.6%

Table II. Average Molecular Weight and Molecular Weight Distribution Index of PVA

AMA (mg)	1# 0	2# 2.0	3# 4.0	4# 6.0	5# 8.0
M_n (×10^{-5})	1.18	1.21	1.29	1.25	1.23
M_w (×10^{-5})	3.16	3.33	3.65	3.57	3.94
M_w/M_n	2.52	2.67	2.83	2.85	3.15

70°C, 80°C, and 90°C to simulate the temperature changes in drilling oil well that was caused by drastic friction.

RESULTS AND DISCUSSION

Molecular weight of all samples was determined by GPC, the results are listed in Table II.

As shown in Table II, we noticed that with the increase of AMA, the number molecular weight change was not obvious, but the molecular weight distribution is becoming wider. The reason is that AMA units supply branch points for the structure of the macromolecule chain. The branch chain length and branch points will influence the molecular weight distribution. The more number of branch points, the bigger influence on molecular weight distribution. If the AMA amount continued to increase, polymer gel will be observed, that is to say, cross-linked polymer occurred, so perfectly control the amount of AMA is quite important.[23] Although by adding suitable chain transfer agent can avoid gel occurring,[24,25] more bifunctional monomer can be introduced, which usually makes final polymer become a wider molecular distribution and lower branch molecular weights to avoid entanglements of long molecular chain, the polymer obtained is usually called hyperbranched polymer.[26] In our experiment, we did not introduce any chain transfer
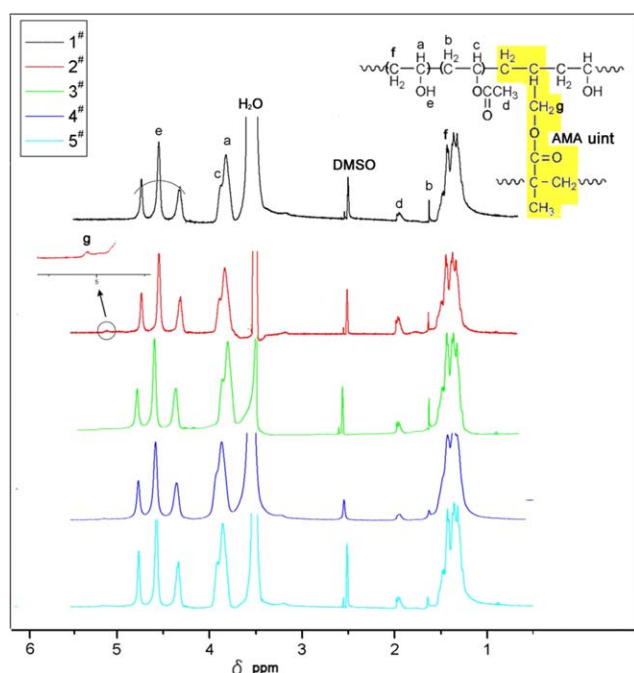

Figure 1. The ^{1}H NMR spectra of all five samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Chemical Shifts for ^{1}H-NMR Spectra in Samples

^{1}H	Chemical shifts (ppm)	^{1}H	Chemical shifts (ppm)
Ha,c	3.80–3.90	He	4.16/4.44/4.70
Hb	1.26	Hf	1.45
Hd	1.87	Hg	5.08

agent, because we do not want to obtain hyperbranched PVA, just want to get small extent branched PVA, which will not change PVA properties too much.

Structure Characterization by NMR

^{1}H NMR spectra were tested of all samples as shown in Figure 1. One can see that there is no big difference. According to the peak d of CH$_3$COO- and the peak e of hydroxyl groups we can obtain the degree of hydrolysis is about 98%.[27,28] Because AMA amount introduced is quite small, so it is not easy to find the characteristic peak of AMA. However, if we amplify the small peak of g (–CH$_2$) at 5.08 ppm, a small peak can be found that proves the existence of the AMA unit. The detail of the shifts was shown in Table III.[27,28]

Changes in the Degree of Crystallinity (X_D)

After introduced AMA, the degree of crystallinity will be changed. DSC tests were determined to calculate the degree of crystallinity. From Figure 2 we can see that the melting peak decreases with AMA increases. According to eq. (1) for calculating the Degree of crystallinity is that:

$$X_D = \frac{\Delta H_m}{\Delta H_m^*} * 100\% \tag{1}$$

The Complete crystal melting heat (ΔH_m^*) of PVA is 152.0 J/g.[29]

ΔH_m stands for the crystal melting heat of the samples.

The degree of crystallinity of the samples were obtained and shown in Table IV. It proved that with the increase of branched points, the degree of crystallinity decreases.

The reason was thought to be that the long branch of the modified PVA is still keeping the same chain structure with the main chain that has a large amount of hydroxyl groups. And the hydroxyl groups in relatively long main chain or branched chain can move and keep close to form hydrogen bonding that makes the degree of the crystallinity of the modified-PVA changed mildly and slightly. As reported, hyperbranched polymer usually has lower crystallinity even totally amorphous although the linear polymer is crystalline polymer, and with the increase of branched points, the polymer has good solubility in solvent compared to the corresponding linear polymer. In our experiments, very small amount of bifunctional monomer was introduced, it is predictable that the branch chain points are

Table IV. Degree of Crystallinity Tested by DSC

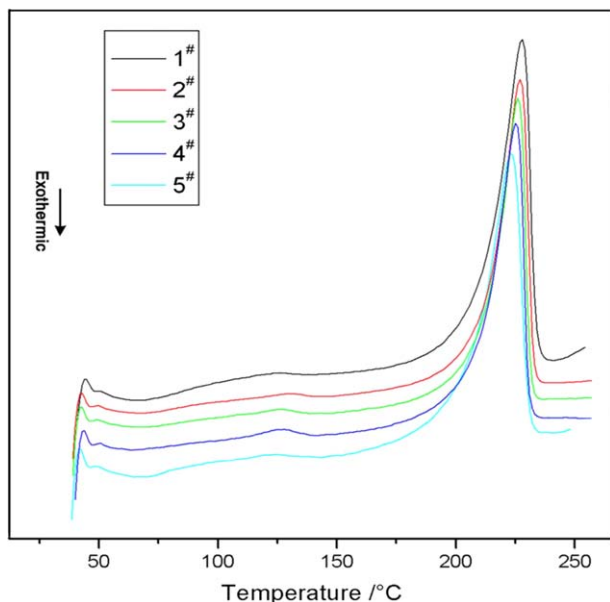| Samples numble	1#	2#	3#	4#	5#
ΔH_m (J/g)	91.5	77.5	74.5	72.8	71.5
X_D	60.2%	51.0%	49.1%	48.1%	47.2%

Figure 2. The DSC curves of all five samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

relatively low and the branch chain is relatively long, the movement of chain is less affected, so the crystallinity did not decrease too much.[30,31]

Changes in Shear Viscosity (η_s)

Figure 3 shows us the changes in shear viscosity. From the picture, the obvious conclusion can be easily obtained, as the addition of AMA increases, the shear viscosity of the solutions increased. That is not consistent with the common principle that the viscosity of the branched polymer is smaller than the linear one at the same molecular weight level in a solution of certain concentration.[12] From the DSC and molecular weight changes, we know that the lightly branched PVA macromolecules with long chain branches have stronger intermolecular
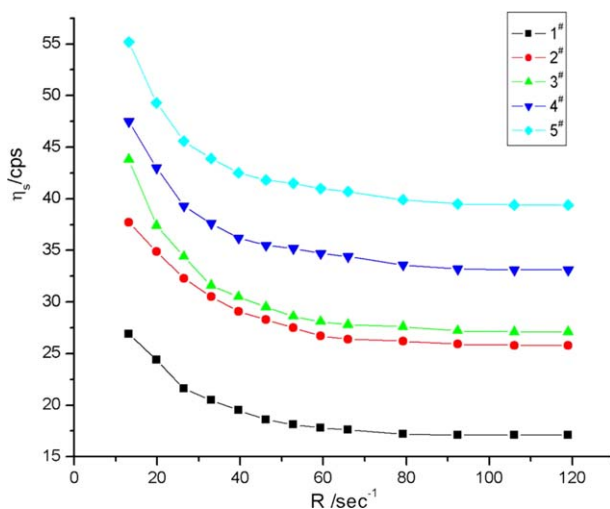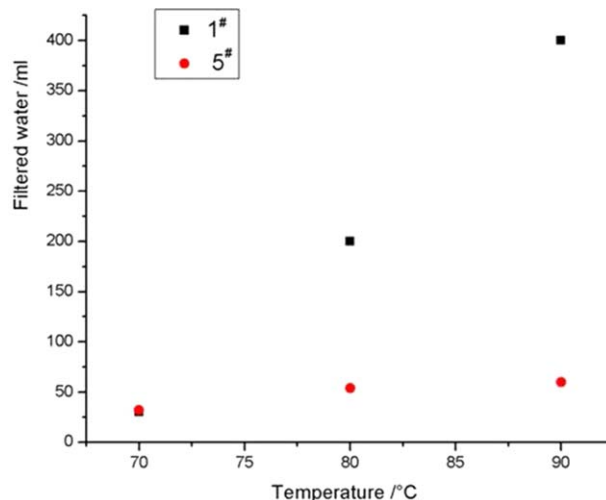

Figure 4. Filtered water of two samples at 70°C, 80°C, and 90°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

forces, which are caused by the heavy entanglement of the branches and main chains. Thus, it is difficult to make the branched PVA molecules have shear-induced alignment.

That is why the branched PVA aqueous solutions have bigger shear viscosity than that of the linear one at the same molecular weight at 20°C. According to the changes in the shear viscosity, it proves that the AMA units are not hydrolyzed, which is consistent with the fact that acrylic ester is not easy for hydrolysis.[31–33] Therefore, the long branches can be saved.

The Water Keeping Ability as Fluid Loss Additive. Samples of 1# and 5# were evaluated by the Static Filtration test for the ability to maintain water at 70°C, 80°C, and 90°C. The results were shown in Figure 4. It is obviously that the branched PVA is better in keeping water than linear PVA.

The reason was thought to be that the long chains of the branched PVA have a great amount of hydroxyl groups that can react with sodium borate to form cross-linked networks. And because of the steady of the branching points, the networks would not be destroyed by the high temperature and the shearing force when the cement slurry is flowing at 80°C and 90°C. Thus, the branched PVA has a better performance in keeping water at 80°C and 90°C as fluid loss additive.

CONCLUSIONS

We introduced bifunctional monomer AMA into polyvinyl alcohol structure to obtain slightly branched PVA. AMA amount cannot be higher because of gel occurring. AMA introduced will decrease the melting peak of branched PVA but without influence on melting point and T_g. Although AMA amount is quite small, when the branched PVA was used as fluid loss additive in drilling fluid, it shows better water keeping ability than linear PVA does when temperature increases. This attributes that the branched chain is helpful for maintain water in the branched network. This kind of branched PVA can be potentially used in oil exploitation for relatively higher temperature condition.

Figure 3. Viscosity changes of all samples in 4 wt % solutions at 20°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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