Evaluation of Polymerization of Polyvinyl Acetate in Methanol and Effect of Alcohols in Branching

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Introduction

Branching of the polymer according to the polymerization are effecting to the polymers nature and polymer solutions even during the numbers of branches, which are relatively small, are effected [1].
The reactions of chain transfer to polymer and terminal double bond polymerization in free radical polymerization create branch in polymers[1,2]. In this investigation the effect of different alcohols in branching of PVAC along with catalyst of AIBN is considered.
for these experimental samples, we use viscometer to find out the change of weight average molecular weight with time is considered and calculation. In term of accurate consideration with usage of the model of moment, effeteness of alcohol's samples in number and weight average branching density, paid at the same time.[3]

Experimental

Materials. The monomer Vinyl acetate(Merk) was distilled under vacuum at the most 24 h before use .the first 20-50 ml of distillate were discarded and was stored at 5 ^{0c} when not in use[4]. Methanol and Isopropyl and AIBN (Merk), were also used as packaged.

Polymerization .Experiment were performed in a four-necked round bottom flask at 60^{0c}, with constant agitation with magnet(300 rpm). The temperature was controlled by means of a heater. The flask, reactor, was washed with THF and dried with acetone before each experiment. The monomer and solvent (less 5-10 mL of solvent used for initiator injection) were introduced into the reactor, heated, and degassed with nitrogen for 10-15 min [3]. The initiator dissolved in the remaining solvent is then injected, at which point .the reaction is assumed to have started[5].

Table 1. parameters for solution polymerization of Vinyl Acetate

Materials	Weight(gr)	Volume(CC)
Methanol	47.52	60
VAC	46.5	50
AIBN	0.07	-

Analytical techniques. The purity of VAC was evaluated by GC. PVAC was also analyzed by by ^{1}H –NMR and ^{13}C-NMR.

Results and discussion

Modeling1. In the classical representation of free radical polymerization kinetics, the rate of reaction in a bath reactor is given by the following expression [6]

$$R_p = -\frac{[M]_0 \partial(1-x)}{\partial t} = k_p [M]_0 (1-x)\left(\frac{2fk_d[I]_0 e^{-k_d t}}{k_t}\right)^{1/2} \quad (1)$$

where $[M]_0$ is the initial monomer concentration, x the conversion, [I] the initiator concentration, k_d the initiator decomposition constant, k_p the propagation constant and f is the initiator efficiency.
The mechanism of polymerization of PVAc have two complex kinetic scheme including polymer transfer and terminal double bond polymerization, one used the method of moments calculation. The weight average branching density given by[4,7]:

$$B_w = \frac{\sum_r \sum_b rbN_{r,b}}{\sum_r \sum_b rN_{r,b}} \quad (2)$$

where $N_{r,b}$ denotes the fraction of polymer molecules with r repeating units and b branch points.

Rate data. Conversion was estimated using the well-known gravimetric technique. Rate data (conversion vs, time) is presented in [**Table 2**], for solution polymerization in Methanol.

Table 2. Tensile tests results for each sample

Solvent	Time(hr)	Conversion(%)
Methanol	0	0
	2.5	28.13
	3.5	39.01
	4.5	46.04
	5.5	47.16

The data regressed using eq(1) are presented in (**Figure 1**).

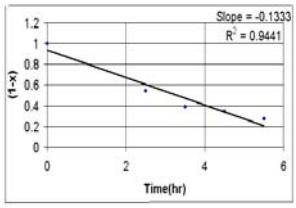

Figure 1. Regression plot for Vac in methanol.

The data regressed using eq.(1) and results showed in (**Table 3**).

Table 3. Flowing tests upon heating of OC120-1

Solvent	$\frac{2fk_d k_p^2}{k_t}$	R_P(1/hr)
Methanol	4.44	0.0901

Results of Modeling. According to the kinetic shown in [**Ref.8**] for polymerization of Vac and equations from as modeling of moment, the result of modelings of branching in [**Figure 2**], is shown as well. MATLAB 6.5 software is used to solve the eq.(2). To compare the branching we used Methanol and Isobutanol of two different kind of alcohol. You will observe the result of modeling in Isobutanol which is point out 'BW' in [**Figure 2**].

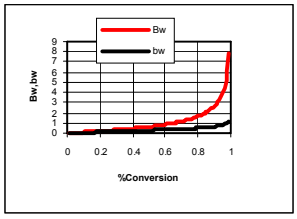

Figure 2. Weight average branching density of two alcohols

Conclusion

In this paper the polymerization of PVAc in Methanol evaluated and the results was gained, also the branching was evaluated to model of moment, the branching of PVAc in Isobutanol is shown more than Methanol. So the solvent which had less chain transfer to solvent, isobutanol, was increased the branching.

References

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