Effect of using batch or semi-batch reactor on the chemical composition distribution of styrene-maleic anhydride-acrylonitrile terpolymers

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Summary

The influence of the reactor type on distribution of chemical composition of ST/AN/MA terpolymers obtained by free-radical polymerization is shown. When a batch reactor was used we have obtained polymers with broad chemical composition distribution. However, if a semi-batch reactor with appropriate addition protocol was used it can be possible to synthesize terpolymers with homogeneous chemical composition.

Introduction

Copolymers of styrene and maleic anhydride have been used as reactive compatibilizers to a large number of immiscible blends. (1-5). Terpolymers of styrene, maleic anhydride and acrylonitrile have great potential as reactive compatibilizers especially for blends which one of the components is nylon. In order to be used as compatibilizer this terpolymer should have a well-defined structure which means to be produced with composition distribution as narrow as possible.

It is a great task to synthesize terpolymers of ST, MA and AN with homogeneous composition by free-radical polymerization since these monomers have very different reactivities. When the reactivities of monomers in free-radical copolymerization are different, the comonomer feed and copolymer composition become different as the reaction proceeds. The more reactive monomer is incorporate preferentially into the first formed copolymer which leads to a change in the copolymer composition as the conversion increases. The result is polymers with large chemical, sequential and molar dispersion.

Preliminary studies with ST-MA-AN terpolymers have demonstrated that MA is the most reactive in this system (6). Azeotropic copolymerization could be the way of preparing copolymers whose composition is exactly the same as that of the comonomer feed (7). However, this terpolymer do not present azeotropic behavior(8). Thus, we have to think in other ways to obtain these terpolymers with homogeneous chemical composition.

This paper shows the cumulative composition distribution of terpolymerization of ST, AN and MA using batch and semi-batch processes in order to evaluate the degree of heterogeneity obtained in these processes.

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Experimental

ST was purified by vacuum distillation and AN was distilled over drops of phosphoric acid. MA was used as received. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. The terpolymerization system ST/AN/MA was investigated experimentally in a batch and semi-batch laboratory-scale vessel. The semi-batch process proceeded by using two addition protocols. AIBN was used as initiator (0.3 mole/%), methylethylketone as solvent (0.76 weight fraction) at 60°C. In the batch process, the reactor was flushed with nitrogen and charged with the prescribed quantities of freshly purified monomers (Table 1), solvent and initiator. In the semi-batch process, the reactor was flushed with nitrogen and the solvent was added. Three separate monomer-initiator batches were prepared according the addition protocol described in Table 1. The three batches were added in succession at a constant rate over a period of 20 min. each. Conversion was determined gravimetrically after the copolymer was isolated by precipitation into methanol. Total nitrogen analysis combined with volumetric titration were used to obtain comonomers fractions in the terpolymer.

Table 1: Charges of ST, MA and AN in terpolymerizations (ST/AN/MA mole ratio in monomer feed: 1:1:1).

MONOMER (g)	BATCH REACTOR	SEMI-BATCH REACTOR					
		PROTOCOL 1			PROTOCOL 2		
		Batch 1	Batch 2	Batch 3	Batch 1	Batch 2	Batch 3
Styrene	4.11	1.37	1.37	1.37	1.37	1.37	1.37
Maleic Anhydride	3.81	1.27	1.27	1.27	0.64	1.27	1.90
Acrylonitrile	2.1	0.7	0.7	0.7	1.05	0.70	0.35

Results

Cumulative composition distributions were evaluated by representing cumulative fractions of total copolymer versus comonomer fraction in the copolymer formed. In order to not favor any of the monomers, the total comonomer mole ratio in the monomer feed was the same in all reactions. Figure 1 presents mole fraction of monomers in cumulative terpolymer by batch process.

According to these results MA was incorporated into the terpolymer during the early stages of polymerization, and the copolymerization rate decreased as the reaction proceeded. This behavior was expected considering MA is the most reactive monomer in this system. Copolymerization rate of ST remained approximately constant during all polymerizations which indicates a high degree of homogeneity in regard to this monomer. AN presented the lowest copolymerization rate, being incorporated into terpolymer below 0.1 mole fraction up to 60 percent conversion. Since the monomer feed contained equimolar quantities of the three monomers at the same time, only the reactivity of the monomers explains these different behaviors.
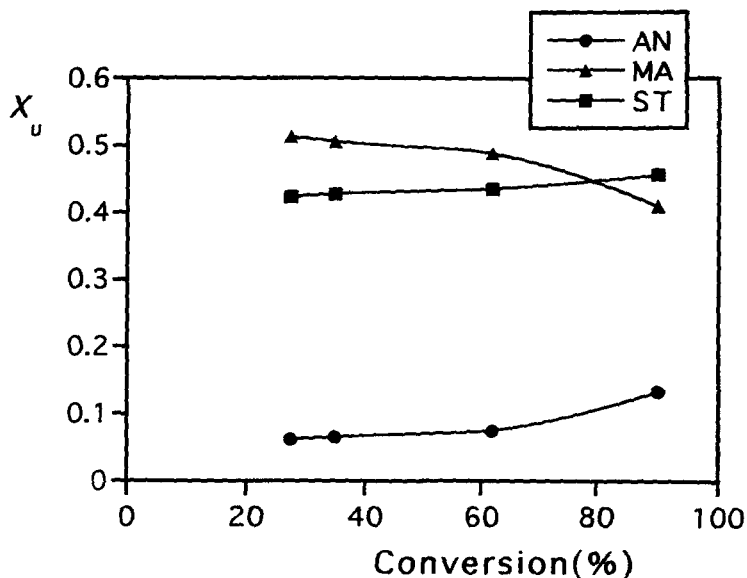
Figure 1: Mole fraction of monomer units (X_u) in total terpolymer versus conversion in batch experiments.

In order to minimize this heterogeneity, we have used the semi-batch process according addition protocol 1 as described in experimental section. The monomer feed composition was the same as used in the batch process. The composition distribution obtained with this process is shown in Figure 2.

As we can see, the differences in copolymerization rate of MA and AN remained. During the earlier stages of polymerization MA was incorporated into the terpolymer faster than the other monomers. The copolymerization rate of MA and ST became approximately the same when the conversion reached 20 percent. AN still has the lowest copolymerization rate among the three monomers. However, by comparing the mole fraction of AN in the total terpolymer synthesized by batch and semi-batch processes (Fig. 3) we can see that AN was incorporated in higher amount in the last one.

Based on this result we have decided to use the semi-batch process with different amounts of monomers in each batch (addition protocol 2). The amount of each monomer in all batches is described in Table 1. According this addition protocol, AN was added to the reactor in decreasings amounts and MA in increasings amounts, but the total mole fraction was held equimolar for all three monomers like in the previous processes. The results of this addition protocol is presented in Figure 4.
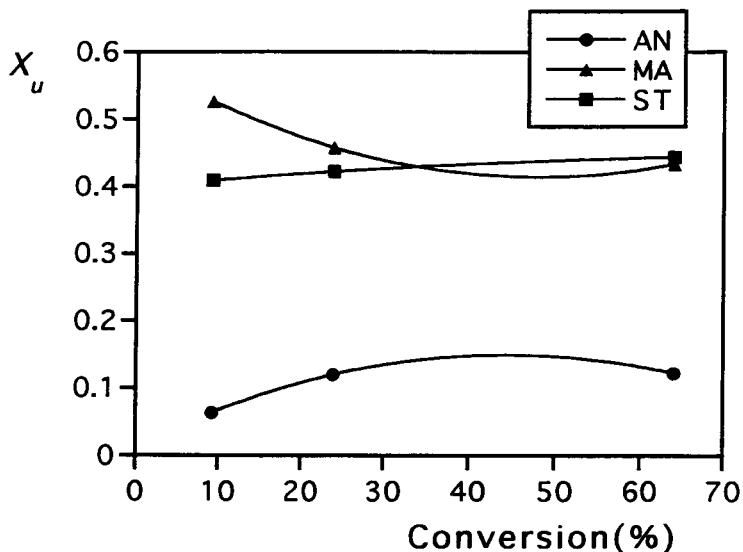
Figure 2: Mole fraction of monomer units (X_u) in total terpolymer as a function of conversion using semi-batch reactor with addition protocol 1. (ST/MA/AN mole ratio in monomer feed:1/1/1).
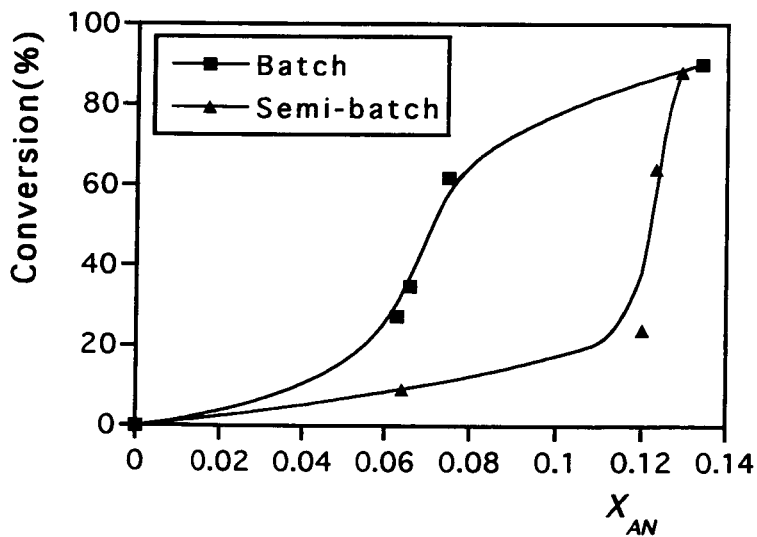

Figure 3: Mole fraction of AN (X_{AN}) in total terpolymer versus conversion using batch and semi-batch reactor.
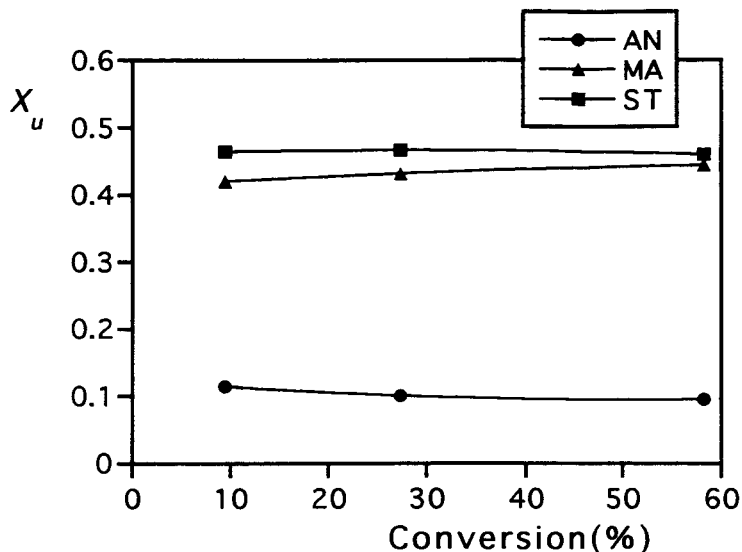
Figure 4: Mole fraction of monomer units (X_u) in total terpolymer as a function of conversion using semi-batch reactor with addition protocol 2. (ST/MA/AN mole ratio in monomer feed:1/1/1.

Although the differences in copolymerization rates between the monomers still remains, the composition distribution became narrow for all monomers. This indicates that each monomer had almost the same copolymerization rate during the course of polymerization. This result becomes even more evident by examining Figure 5 which shows a comparison between the mole fractions of AN and MA in total terpolymer versus conversion using semi-batch reactors with both addition protocols, 1 and 2. As we can see the mass balance helps the less reactive monomer (AN) to be incorporated into the terpolymer faster and in a higher amount. The terpolymerization of ST, MA and AN by semi-batch reactor and the monomer addition protocol 2 is a good process to obtain terpolymers with homogeneous composition. This way, we are able to control the composition of these terpolymers by using a very simple polymerization process with very good reproducibility.
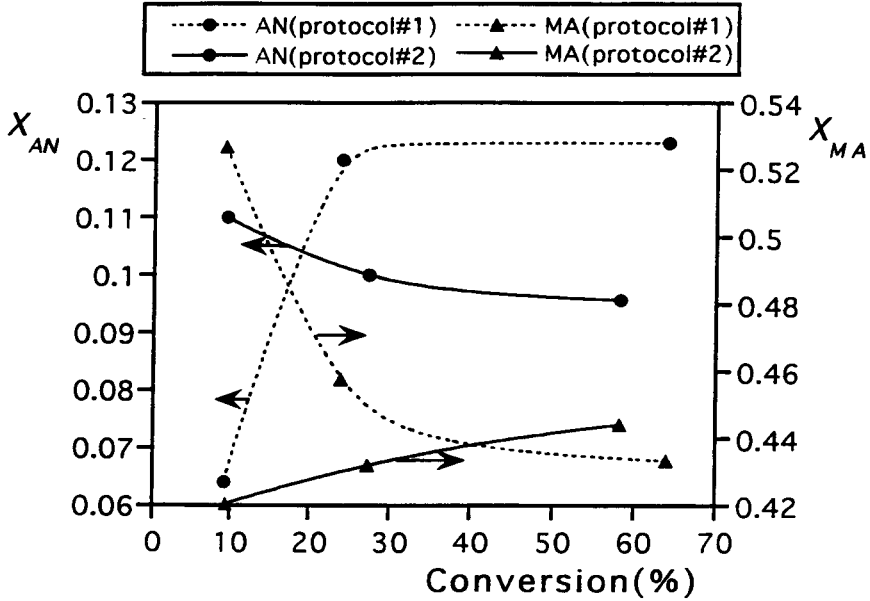
Figure 5: Mole fraction of AN (X_{AN}) and MA (X_{MA}) in total terpolymer as a function of conversion using semi-batch reactor (addition protocol 2).

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