Preparation of alkyl acrylate-acrylic acid copolymers by simultaneous hydrolysis and polymerization

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Summary

The ability of concentrated nitric acid (65% HNO_3) to initiate reactions of polymerization when in contact with acrylic and methacrylic acids and esters at room temperature in the absence of other reagents has been studied in this laboratory. In a previous paper, we presented the results when the reaction was applied to methacrylic monomers. This work reports data obtained with methyl and ethyl acrylates; high molecular weight ester-acid copolymers were produced. The nature of the products and the course of the reaction are discussed.

Introduction

The action of nitric acid on acrylic and methacrylic monomers is reported in the literature (1-15). Pistoia et al. describe the electroinitiated bulk polymerization of acrylonitrile(AN) at about 25°C in the presence of fuming nitric acid containing 4% N_2O_4 (w/w), by a free-radical mechanism (1). Methyl methacrylate(MMA) polymerization in a similar system at temperatures in the range 5 to 60°C is also reported (2). Acrylamide(AM) polymerization was extensively studied by Bhadani and coworkers: in DMF solution at 25°C, in the presence of nitrogen dioxide (3); in DMF or water solution at 40-50°C, with nitric acid, using also MMA as comonomer (4); in DMF at 60°C, with 100% pure nitric acid, in homopolymerization or copolymerization with AN (5); in aliphatic alcohols at 40°C, in the presence of nitrogen dioxide (6); in DMSO at 50°C, with 100% pure nitric acid (7). MMA is reported to polymerize in DMSO solution at 50°C in the presence of nitrogen dioxide (8). In all cases high molecular weight polymers are obtained and a free-radical mechanism is admitted to operate.

In previous work in this laboratory we described high molecular weight copolymers MMA-MAA obtained from a heterogeneous mixture of MMA and 65% nitric acid at 25-40°C (9-15). The present paper describes this reaction using the analogous acrylic esters, MA and EA, under the same conditions, with particular attention to the ester hydrolysis which occurs simultaneously in the acid medium.

Experimental

The monomers were distilled before use. Nitric acid p.a. (65% HNO_3) was used as received. The reactions were run under nitrogen in 200 ml glass stoppered vials, protected from light, immersed in a thermostatic bath. The experiments were run at the molar ratios monomer:HNO_3:H_2O 1:1.5:2.5 , 1:7.5:12.5 and 1:15:25, at 25, 30 and 40°C. The reaction was stopped pouring the mixture into 10 times the volume of cold water. The product precipitated as a rubbery to vitreous mass depending on the molar ratios. The residual nitric acid was eliminated by successive washings with distilled water. The polymer was purified at least three times through dissolution in methanol and precipitation on cold water. Finally, the product was vacuum dried at room temperature to constant weight. The products were characterized by IR,^{13}C NMR, DSC, viscosity and volumetric titration. The molecular weight was determined using dioxane as solvent. The carboxyl groups were determined by dissolving the samples in methanol, adding 0.05 N NaOH solution in ethanol and back-titrating the excess with 0.05 N HCl solution in ethanol.

Results and Discussion

The experimental results showed that, surprisingly,the yields in the reaction of acrylic esters with concentrated nitric acid were much higher without stirring (Figure 1); up to 95% and 80% conversion were obtained with MA and EA, respectively, after 48 h, 1:1.5:2.5 monomer:HNO_3:H_2O ratio, at 25°C as shown in Figure 2. It is interesting to notice that in the same condition, no polymer is formed with MMA, as reported in our previous paper (15)and the order of reactivity, according to the polymer yield, is: AA> MAA> MA> EA> MMA.

It was observed that the higher the amount of nitric acid and the higher the temperature, the worse conversion results.
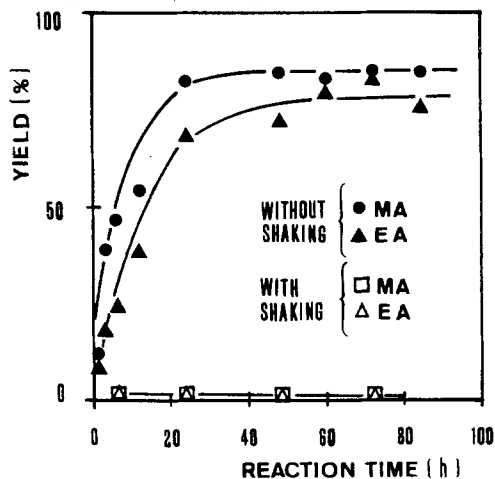

Figure 1
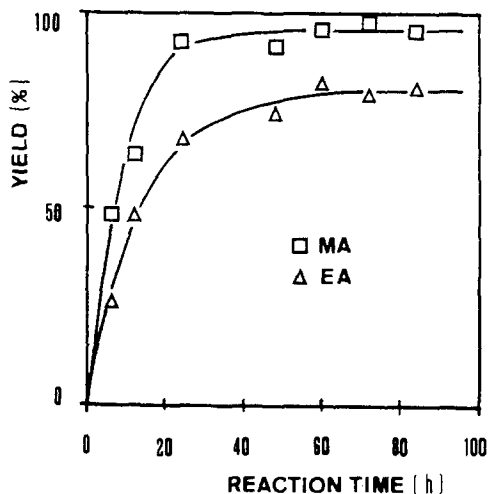Formation of polymer with acrylic ester at 30°C monomer:HNO_3:H_2O molar proportion 1:1.5:2.5

Figure 2
Formation of polymer with acrylic ester at 25°C mo-
nomer:HNO_3:H_2O molar proportion 1:1.5:2.5

     The reaction products form very viscous solutions; the
resulting cast films are colorless, transparent and flexible.
This suggests low-crystalline, high molecular weight polymers.
Both series of polymer products showed the same solubility
behavior: soluble in methanol, acetone, dioxane, DMF, DMSO
and 1% sodium hydroxide aqueous solution; insoluble in water,
hexane and chloroform; partially soluble in benzene and THF.
     It is interesting to notice that, under the same con-
ditions, the homopolymers PMA, PEA and PAA showed different
solubility than the reaction products what allowed the puri-
fication procedure to remove the homopolymers from the copo-
lymer reaction products. The changes in solubility indicate
partial hydrolysis.
     Spectra IR and ^{13}C NMR showed absorptions and signals
correspondent to ester and acid groups for both MA and EA
reaction products. No anhydride group was detected. GPC ana-
lysis showed a broad peak as expected much alike previous
data for MMA products (15). These experimental results indi-
cate that a copolymer ester-acid is formed in all cases. The
COOH groups were determined by titration; the results were
consistent with previous analytical indications as shown by
Figure 3 and Figure 4. The percentage of acid units in the co-
polymer products is shown in the darker area under the curve
and indicates that there are simultaneous reactions of poly-
merization and hydrolysis; the longer the reaction time, the
higher acid content in the copolymer. Calorimetric analysis
(Figure 5) confirmed that T_g increases as the hydrolysis degree
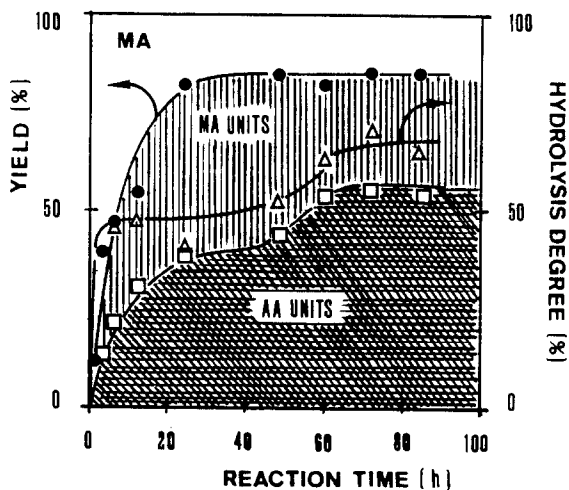increases, as expected.

Figure 3
Composition of MA and AA units in the polymer from
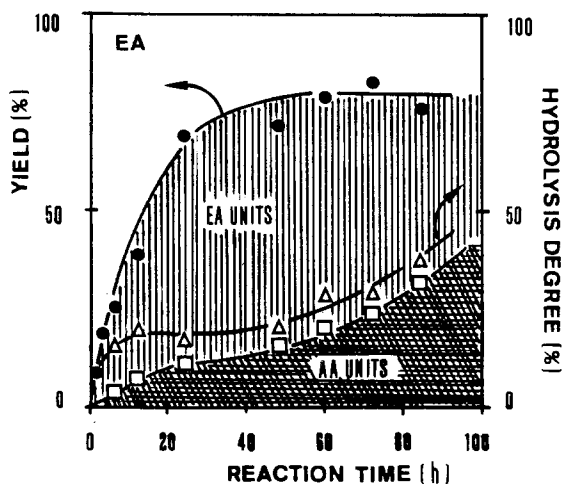the mixture $MA:HNO_3:H_2O$ 1:1.5:2.5 at 30°C

Figure 4
Composition of EA and AA units in the polymer from
the mixture $EA:HNO_3:H_2O$ 1:1.5:2.5 at 30°C

The molecular weight was evaluated from viscosity data.
In dioxane, which is a good solvent for all polymers, the
constants for PAA are (16): $K = 76 \times 10^{-5}$ dl/g and a = 0.50.
It was shown that, for MMA-MAA copolymer, there was not a lar-
ge variation in M_w when the copolymer was totally esterified
and the proper constant were applied – what means, not a lar-
ge error was introduced using the ester viscometric constants

to evaluate the M_w of the copolymer (15). This assumption was taken to estimate the average size of the macromolecular ester-acid products as 10^5-10^7. The molecular weight increases fast in the beginning of the reaction, reaches a plateau and decreases slowly as the reaction time is extended.

To correlate the experimental results, it is important to consider that the concentrated nitric acid has a double role as a hydrolytic reagent and as a source of the paramagnetic species NO and NO_2. Both oxides are present in the nitric acid concentrated aqueous solution, depending on the temperature. The acid hydrolysis of ester groups, either in the monomer or in the polymer, plays an important role in the overall reaction. The polymerization process is free-radical initiated as could be expected and was confirmed by the inhibiting/retarding effect of picric acid in the formation of polymer.

Figure 6 represents the progress of the reaction in the mixture of MA and concentrated nitric acid in which the proportion is $MA:HNO_3:H_2O$ 1:1.5:2.5, at 30°C. It shows clear evidence of three different types of reaction which are involved in the formation of acrylic ester-acid copolymers: the acid hydrolysis of ester monomer; the copolymerization by free-radical mechanism; and the hydrolysis of the pendant ester groups in the polymer. It is possible to visualize that hydrolysis of the ester monomer occurs at the beginning of the reaction, and reaches a plateau between 24-50 hours. After that the hydrolysis of pendant ester groups in the polymer becomes more important and other plateau is reached.
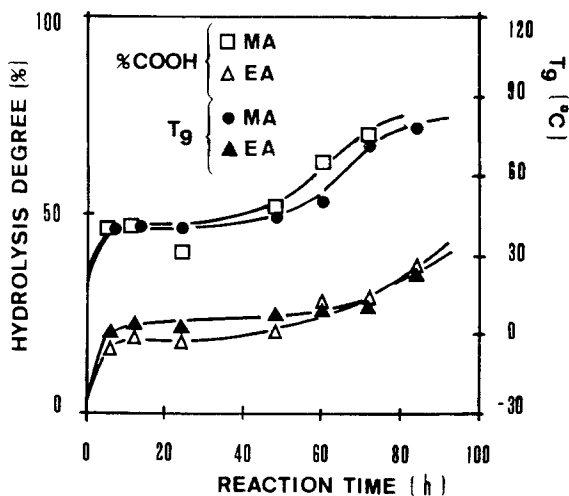

Figure 5
Hydrolysis degree and T_g vs reaction time of polymer product monomer:HNO_3:H_2O molar proportion 1:1.5:2.5 at 30°C
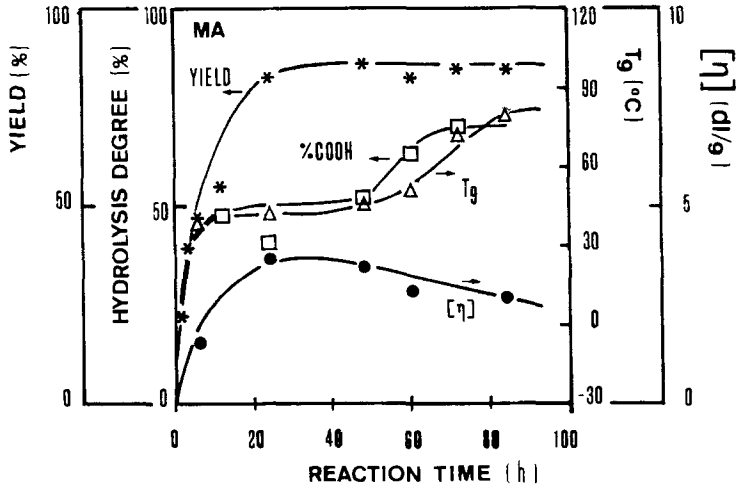
Figure 6
Progress of the reaction in the mixture $MA:HNO_3:H_2O$
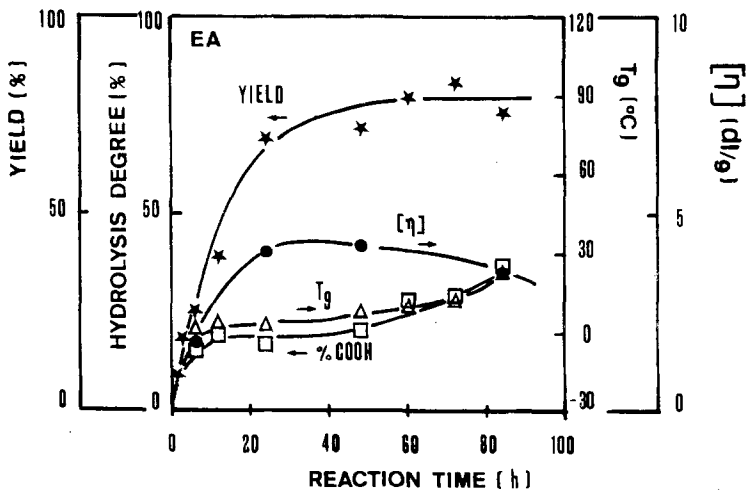1:1.5:2.5 at 30°C

Figure 7
Progress of the reaction in the mixture $EA:HNO_3:H_2O$
1:1.5:2.5 at 30°C

The acid hydrolysis of the ester groups in both ca-
ses seems to follow an $A_{AC}2$ mechanism (17-27). According to
experimental data (28), MA hydrolysis is faster than EA, either
in the monomer or in the pendant ester groups in the polymer.
The same behavior was observed for the reaction of EA with
concentrated nitric acid in which the proportion is $EA:HNO_3:$
H_2O 1:1.5:2.5 run at 30°C, but at slower rates, as can be
seen in Figure 7.

Acknowledgment

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504

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