Polymer Bulletin

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Copolymerization of N-tert-butyl Acrylamide with Acrylonitrile and with Methyl Methacrylate

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SUMMARY

The reactivity ratios for the radical copolymerization of N-tert-butyl acrylamide with acrylonitrile and with methyl methacrylate were determined at 60° C.

INTRODUCTION

Many N-alkyl acrylamides have been synthesized and characterized (MARK et al., 1964). No information, however, has been disclosed on the copolymerization of these monomers with acrylonitrile (AN) except with N-octadecyl acrylamide (JORDAN and WRIGLEY, 1964). It is expected that some of the N-substituted acrylamides may be used as promising comonomers in the manufacture of acrylic fibers (cit. MARK). In this paper the copolymerization of AN with N-tert-butyl acrylamide (tBuAM) is reported. In addition, the copolymerization of methyl methacrylate (MMA) with tBuAM has been evaluated.

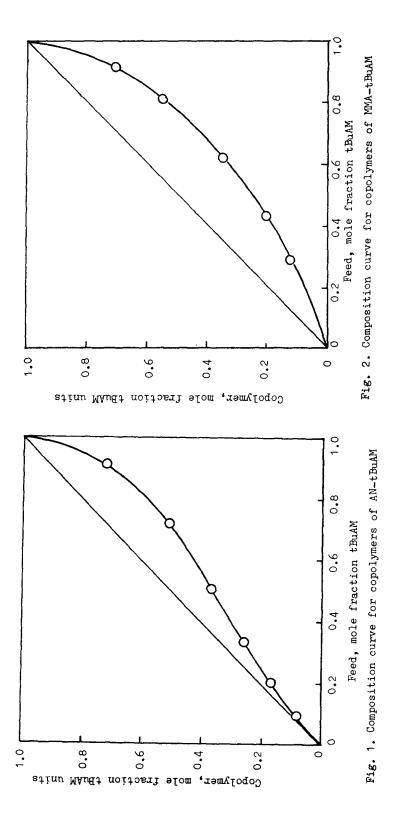
EXPERIMENTAL

N-tert-butyl acrylamide was prepared by reaction of AN and tert-butyl alcohol in the presence of sulfuric acid (PLAUT and RITTER, 1951). The product was recrystallized twice from benzene, m.p. 128-129°C. AN and MMA were purified according to the usual methods. Dimethyl sulfoxide was destilled before use and azobisisobutyronitrile (AIBN) was recrystallized from ether. The other reagents were analytical pure grade.

Copolymerizations were carried out under nitrogen in sealed tubes at 60°C, with 0.4 wt% AIBN. They were precipitated twice from a water-methanol mixture.

The copolymerization of tBuAM with AN was carried out in dimethyl sulfoxide, the copolymerization with MMA in ethyl alcohol.

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RESULTS AND CONCLUSIONS

The reactivity ratios were determined by both the Fineman-Ross plot (FINEMAN and ROSS, 1950) and the intersection method (ALFREY et al., 1952). For AN (M_1) with tBuAM $r_1 = 1.14 \pm 0.02$ and $r_2 = 0.20 \pm 0.02$ were found, for MMA (M_1) with tBuAM $r_1 = 2.83 \pm 0.03$ and $r_2 = 0.25 \pm 0.02$.

The Alfrey Price Q-e values for tBuAM, calculated from the monomers reactivity ratios, are 0.17 and -0.11 respectively.

These results when compared with the data for N-tert-octyl acrylamide and N-octyl acrylamide support the observation that branching on the alkyl substituent has little influence on the polymerization characteristics of N-alkyl acrylamides (BORK et al., 1963).

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Received February 10, 1981 Revised March 7, 1981 Accepted March 11,1981