Notes

Radical Copolymerization of *N*-(β-Propionamido)acrylamide

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In the course of some work on the base-catalyzed hydrogen migration polymerization of acrylamide to poly(β-alanine), we obtained in high yield the *N*-(β-propionamido)acrylamide (or acrylamide dimer)[1] having the formula CH_2=CHCONH-$CH_2CH_2CONH_2$; this product has been already obtained by other authors.[2,3]

This monomer, which can be regarded as a N-monosubstituted acrylamide, can be polymerized by free radical polymerization thus obtaining homopolymers and copolymers which are useful for photographic applications.[4,5] In the present note the results obtained in the copolymerization of this monomer with styrene are reported; for comparison acrylamide has been copolymerized under same conditions.

The *N*-(β-propionamido)acrylamide (acrylamide dimer, AMD) was obtained according to the reported conditions[4] by treating *n*-butyllithium with acrylamide in dioxane at room temperature. The product was recrystallized twice from dioxane before polymerization.

Anal. Calcd for $C_6H_{10}N_2O_2$: C, 50.65; H, 7.03; N, 19.70. Found: C, 50.5; H, 7.0; N, 19.45. A 1-g sample of the product (mp 149–150°) absorbed 1.11 g of bromine (calcd for $C_6H_{10}N_2O_2$, 1.125 g).

Styrene (ST) and acrylamide (AM) were trade products. ST (Montedison) was purified by distilling before polymerization according to the usual techniques. AM (Nymco) was recrystallized from chloroform and accurately dried before polymerization. Dioxane and ethanol were reagent grade products and were dried and distilled according to the usual techniques. The initiator, α,α′-azobisisobutyronitrile (Fluka), was crystallized twice from ethyl ether.

TABLE I[a]

f_1	% N in copolymer	F_1
	Acrylamide (M1)–styrene (M2)	
0.1	1.28	0.092
0.2	2.06	0.146
0.4	5.24	0.346
0.5	6.68	0.429
0.5	6.79	0.435
0.6	8.36	0.519
0.7	9.95	0.599
0.8	12.83	0.732
0.9	15.58	0.847
	N-(β-Propionamido)acrylamide (M1)–styrene (M2)	
0.1	1.45	0.055
0.2	3.06	0.119
0.4	9.15	0.389
0.5	10.36	0.448
0.6	12.20	0.540
0.7	13.17	0.596
0.9	17.80	0.871

[a] The copolymerizations have been carried out in a mixture of dioxane–ethanol (70–30 by volume) at 70°. The total monomer concentration has been kept constant at 0.4 mol/l. of solvent. The initiator α,α′-azobisisobutyronitrile was used in the amount of 1 g/l. of solvent.

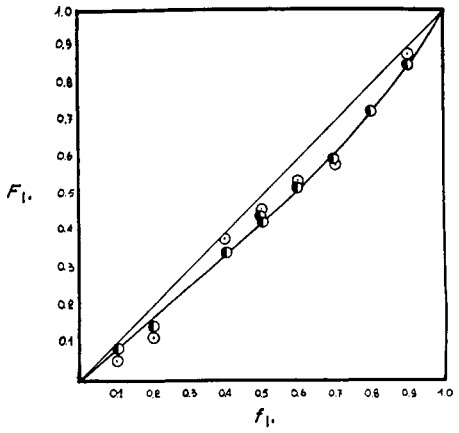

Figure 1. ⊙, AMD – ST; ◐, AM – ST (calculated curve for $r_1 = 0.59$, $r_2 = 1.13$); (solvent, dioxane–ethanol (mixture 70–30 v/v); see Table I.

All experiments were performed in a glass tube which was filled with dry monomers, solvents, and initiator. The tube was then sealed in a nitrogen atmosphere and heated at 70°. All the copolymerizations were stopped by pouring the tube contents into an excess of nonsolvent, obtaining in each case yields lower than 10%. The total monomer concentration was kept constant at 0.4 mol/l. of solvent; a mixture of dioxane–ethanol (70–30 by volume) was used as solvent. The initiator was used in the amount of 1 g/l. of solvent (see Table I).

The copolymers were precipitated in methanol or in acetone; they were redissolved and reprecipitated, washed, and accurately dried. The copolymer compositions were determined on the basis of their nitrogen contents. The analyses were carried out by the semimicro Kjeldahl method on products previously dried under reduced pressure to a constant weight.

Table I shows the experimental values obtained for the systems AM–ST and AMD–ST. The monomer f_1 and copolymer F_1 compositions are expressed as molar ratios with respect to AM and AMD. Figure 1 shows the copolymerization curve calculated for $r_1 = 0.59$ and $r_2 = 1.13$ of the system acrylamide–styrene. The r_1 and r_2 values have been obtained by the Fineman and Ross method and checked by the intersection method according to Mayo and Walling. The corresponding $Q_1 = 0.54$ and $e_1 = -0.17$ values for AM have been calculated on the basis of reference values of $Q_2 = 1$ and $e_2 = -0.8$ for ST.

The calculated curve is in good agreement with the experimental data. Figure 1 reports also the experimental values found for the system AMD–ST. As shown, the copolymerization behavior of AMD, at least under our experimental conditions, does not differ remarkably from that of acrylamide. It seems therefore that the substitution of a hydrogen atom with a propionamido group on the nitrogen of acrylamide does not affect too much the behavior in the copolymerization.

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