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Acrylamide-Styrene Copolymerization with the 4,4'-Azo-Bis-(4-Cyanovaleryl)-Bis-(m-Chlorobenzoyl) Diperoxide Azoperoxy Initiator

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SUMMARY

The copolymerization of acrylamide with acrylic acid by use of 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide as initiator was studied. The thermolysis or photolysis of the mentioned initiator was studied. The thermolysis or photolysis of the mentioned initiator was used to prepare polystyrene with final peroxidic groups, which was further reacted with acrylamide to yield poly(styrene-acrylamide).

INTRODUCTION

Bifunctional initiators, possessing labile groups with different stabilities, assure a constant concentration of radicals in the polymerization process, permitting thus the formation, in the first stage, of a macromolecular initiator which, together with a new monomer, is capable of forming blockcopolymers. A series of previously synthesized peroxy initiators proved to be adequate in the synthesis of some MMA-St based (SCHULZ et al., 1974; SIMIONESCU et al., 1983; 1984; PIIRMA et al., 1979) and MMA-AN based (SHAIKH et al., 1980) blockcopolymers.
The present paper describes the copolymerization of acrylamide (AA) with acrylic acid (AcA), as well as the blockcopolymerization of styrene (St) and acrylamide, in the latter case the PSt and PAA with peroxy final groups being used as macromolecular initiators. They have been synthesized by the polymerization of the respective monomers with the azoperoxy initiator having the structure of a 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide, the homolysis of which has been performed both thermally and photochemically (KIM GYU et al., 1984).

EXPERIMENTAL

Copolymerization and blockcopolymerization have been conducted in solution, in closed glass ampoules. The polymerization duration was set according to the experimental schedule. After polymerization, the ampoules have been suddenly cooled, whereas the reaction mixture was purified by the extraction of the unpolymerized monomers with specific solvents.
The amount of polyacrylamide from the reaction mixture and the monomer in the copolymer has been determined by nitrogen analysis (the Kjeldhal method). The determination of the peroxy groups from PSt has been performed by the iodometric method.

RESULTS AND DISCUSSION

Copolymerization of acrylamide with acrylic acid. The copoly-

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merization of AA which AcA has been performed in dioxane solutions, at variable AA/AcA molar ratios (Figure 1). At the initiator photolysis, UV large spectrum (200 - 400 nm) radiations have been used, at a temperature of 20°C. Depending on the ratio of the two monomers, the results showed in Table 1 have been obtained.

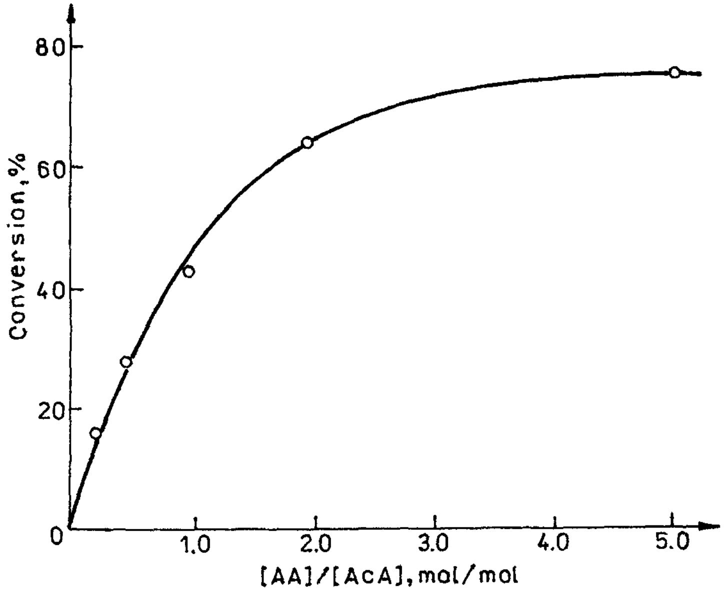


Figure 1. Variation of conversion in copolymer at different comonomer ratios.

TABLE 1
Acrylamide - acrylic acid copolymerization with the 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide initiator

AA/AcA ratio	Conversion	$[\eta]$	$\bar{M}^*$	Copolymer composition	
				AA	AcA
(mol/mol)	(%)	(dl/g)		(%)	(%)
0.2	15.6	4.03	1015300	25	75
0.5	27.1	2.49	556176	38	62
1.0	47.2	2.96	690364	51	49
2.0	63.8	4.38	1126694	63	37
5.0	74.8	4.54	1178374	78	22

*Calculated with k, α for polyacrylamide.

The increasing of the AA concentration in the system permits higher conversions.

The composition plotting for the comonomers system under study (Figure 2), as well as the values of the copolymerization constants, determined by the Kélén - Tüdös method (Figure 3) ($r_1 = 0.556$, $r_2 = 0.586$) show that the polymerization reaction is of the azeotropic type, the two monomers having close values.

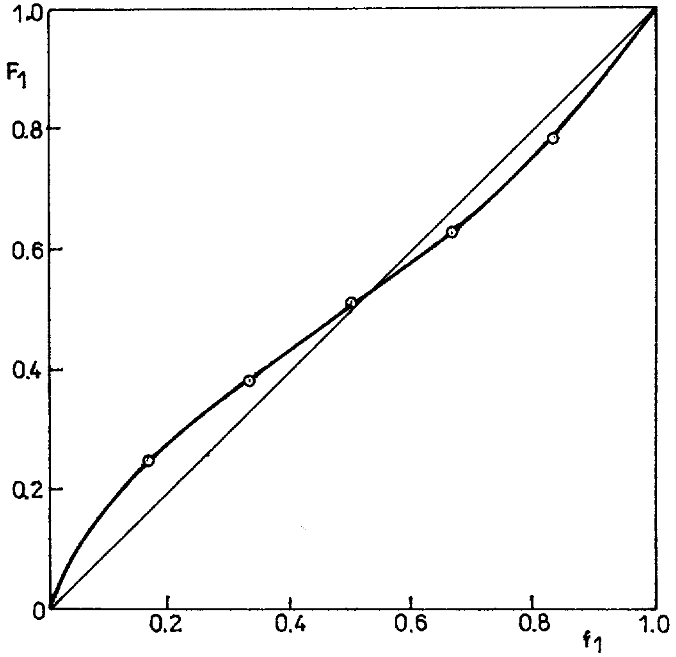


Figure 2. Copolymerization diagram of AA (M_1) - AcA (M_2) system.

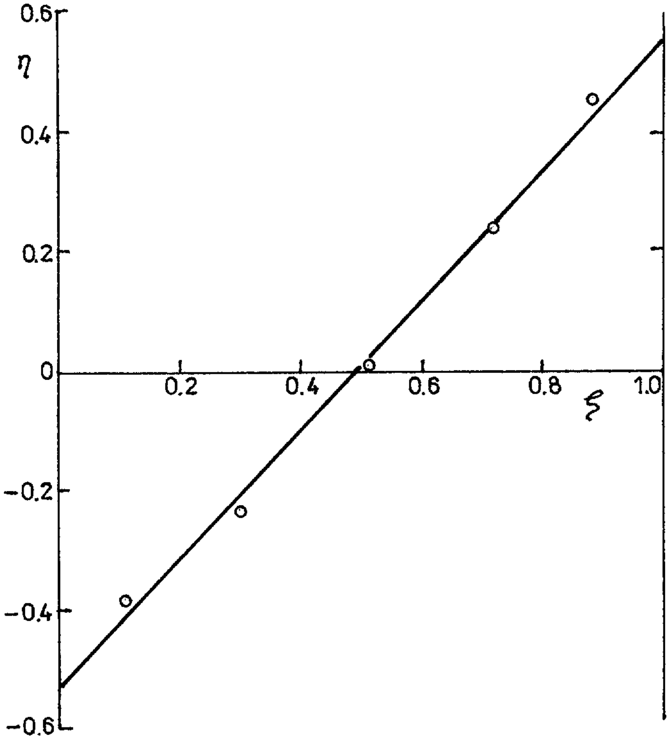


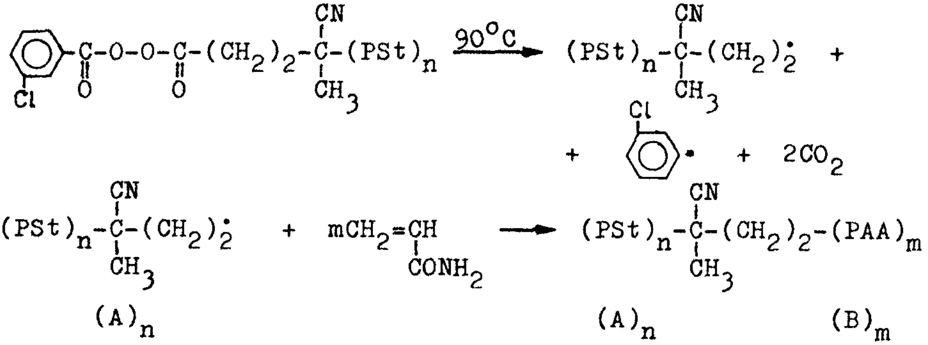
Figure 3. The Kélén-Tüdös plot of AA (M_1)-AcA (M_2) system.

In accordance with the general copolymerization theory, the process may be conducted even at conversions higher than 10%, up to 50% for the type of monomer under discussion, and without affecting the copolymer composition. Values comparable with those obtained in the case of using the already mentioned azo-peroxy initiator are recorded in literature too (WALZ et al., 1977).

Styrene-acrylamide blockopolymerization with macromolecular polyacrylamide and polystyrene based initiators. The polystyrene initiator has been obtained by the polymerization of styrene with 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide initiator. The reaction was performed in conditions that assured the maintaining of the peroxy group in the polystyrene chain.

In the first stage, the thermal polymerization has been performed at a temperature of 60°C, whereas the photochemical one, with UV radiation (λ = 366 nm). The two types of polymerizations have been followed at different concentrations of the initiator and different polymerization times.

The blockcopolymerization has been performed by the addition of the second monomer in the PSt initiator solution in benzene or in dioxane. AA was used as a second monomer, the polystyrene peroxy groups being splitted at 90°C. Such a temperature assures a total decomposition of the O-O links, as showed by the kinetic data obtained for the initiator thermolysis (SIMIONESCU et al., 1984b). The polymerization termination occurring by recombination, the obtained blockcopolymer has the following structure:

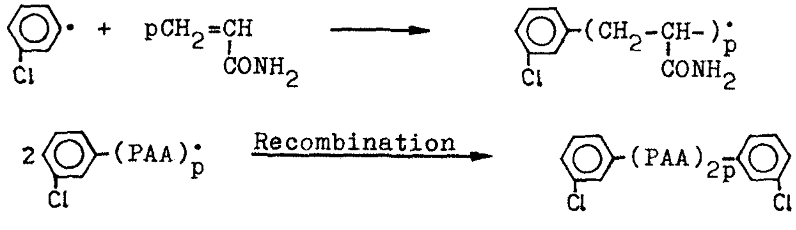


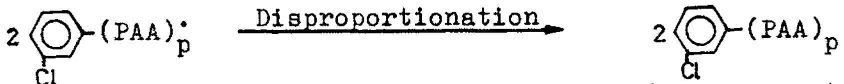
$$2(A)_n-(B)_m^{\bullet} \xrightarrow{\text{Recombination}} (A)_n-(B)_{2m}-(A)_n$$

whereas, for disproportionation:

$$2(A)_n-(B)_m^{\bullet} \xrightarrow{\text{Disproportionation}} 2(A)_n-(B)_m$$

The blockcopolymerization includes the following secondary reactions:





The block copolymer - homopolymer mixture has been separated by the selective extraction method, according to the following scheme:

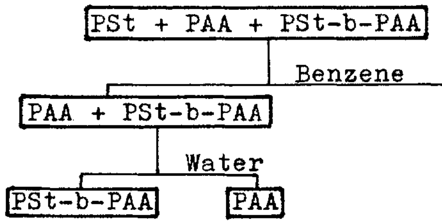


TABLE 2
Peroxy group content of the polystyrene initiator

Polymerization method	Initiator concentration (10^3 mol/l)	Time (h)	$\tilde{M}$	Final peroxy groups (10^5mol/g)	(mol/mol PSt)
Initiator photolysis $\lambda = 366$ nm	6.5	20	42625	14.5	6.3
Initiator thermolysis (60°C)	3.5	3	28018	10.68	9.4
	6.5	3	56601	10.35	5.8
	13.3	3	30187	13.04	3.9
	3.5	5	106607	6.44	6.9
	6.5	5	56806	8.46	4.8
	13.3	5	31432	10.37	3.3
	3.5	7	111982	5.54	6.2
	6.5	7	77679	5.64	4.4
	13.3	7	39775	5.96	2.4

The compositions of the reaction mixture, as well as those of the blockcopolymer, are presented in Table 3.

TABLE 3
Blockcopolymerization of the PSt initiator, obtained by the initiator photolysis (UV radiation, $\lambda = 366$ nm) with acrylamide, at different PSt/AA ratios

PSt/AA ratio	Composition of the reaction mixture			Blockcopolymer composition
	PSt	PAA	PSt-b-PAA	PAA
(mol/mol)	(%)	(%)	(%)	(%)
0.25	20.2	62.2	17.6	34.4
0.67	41.8	39.1	19.1	29.3
1.50	60.0	21.6	18.4	33.6
4.00	77.5	2.8	19.7	12.8

T = 90°C; Concentration of the reactants = 1 mol/l; Time = 7 h; initial M PSt = 4.3 x 10^4; solvent = dioxane.

Data presented in Table 3 show that, simultaneously with the increasing of the amount of PSt initiator in the polymerization system, the polyacrylamide ratio in the blockcopolymer decreases. The molecular weight of the PSt initiator (Table 4) does influence the yield and the composition of the blockcopolymer, which is modified at the same time with the composition of the reaction products.

TABLE 4

Blockcopolymerization of the PSt initiator obtained by the initiator photolysis (UV radiations, λ = 366 nm) with AA, depending on the molecular weight of the PSt initiator.

M PSt initiator x 10^{-4}	Composition of the reaction product (%)			Blockcopolymer composition (%)
	PSt	PAA	PSt-b-PAA	PAA
2.0	11.3	44.6	44.1	72.1
3.0	12.0	46.5	41.5	69.9
3.6	10.3	49.1	40.6	68.9
4.0	19.3	53.1	27.6	65.7

T = 90°C; PSt/AA ratio = 0.34 mol/mol; Solvent = benzene; Concentration of the reactants = 0.15 mol/l.

The blockcopolymer ratio in the mixture, as well as the PAA ratio in the macromolecular chain decrease simultaneously with the increase of the molecular weight, as a consequence of the decrease of the concentration of peroxy groups introduced in the system.

The blockcopolymerization process is also influenced by the solvent nature; thus, benzene is more favourable to the development of the reaction, as compared to dioxane, although the reactants are better soluble in the latter one.

CONCLUSIONS

1.Copolymerization of AA and AcA has been performed by the photolysis of the 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide initiator.

2.The influence of the ratio between the monomers has been followed, respectively the increase of the acrylamide concentration in the system on the process development.

3.The monomer composition plotting and the values of the copolymerization constants emphasize to the azeotropic character of the reaction.

4.With a view to obtain poly(styrene-b-acrylamide), a polystyrene macromolecular initiator with peroxy groups has been firstly prepared, thermally and photochemically, by the polymerization of styrene, in the presence of the mentioned azo-peroxy initiator.

5.By the nitrogen method (Kjeldhal) the composition of the reaction mixture and of the blockcopolymer has been determined, depending on the PSt/AA ratio, as well as on the initiator PSt molecular weight.

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