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Initiators

Bifunctional Initiators

7. Acrylamide Polymerization with 4,4'-azo-bis-(4-Cyanovaleryl)-bis-(m-Chlorobenzoyl) Diperoxide as Initiator

Kim Gyu Sik[2], Severian Dumitriu[1], Eugenia Comăniţa[1], and Cristofor Simionescu[1]

[1] Department of Organic and Macromolecular Chemistry, Polytechnic Institute of Jassy, R-6600 Jassy, Romania

[2] Chemical Engineering Institute, Hamhîn, D.P.R. Korea

SUMMARY

Acrylamide was polymerized by both thermolysis and photolysis of the 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide as initiator. The molecular weight and the conversion depend on polymerization duration and initiator concentration. The sequential character of the initiator was proved by the two stage polymerization of acrylamide when the obtained molecular weights were twice as compared to those of the one stage process.

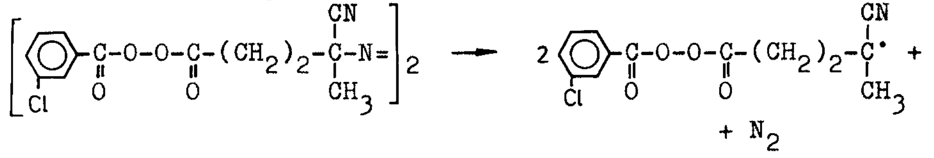
INTRODUCTION

The bi- and polyfunctional initiators containing labile groups of different thermostabilities are suitable for two-stage polymerizations. First, an active polymer with labile groups is prepared (macromolecular initiator) which acts as initiator for the second monomer in the following stage. The two-stage polymerization gives the possibility of a rather simple obtaining of blockcopolymers and polymers of high molecular weight. A series of azo peroxide initiators, some derivatives of the 4,4'-azo-bis-(4-cyanovalerianic) acid were used in the polymerization of styrene (SIMIONESCU et al., 1983; SHAIKH et al., 1980; SIMIONESCU et al., 1984a), methyl methacrylate (PIIRMA et al., 1979) and other vinylic monomers (ANAND et al., 1982; GUNESIN et al., 1981; BILINA et al., 1977). The obtained polymers are macromolecular initiators for the synthesis of blockcopolymers whose structure depends on peroxy end group content as well as on the reaction time, temperature, polymer/monomer ratio.
The kinetic data (SIMIONESCU et al., 1984b) on the thermolysis and photolysis of the 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl) diperoxide as initiator are indicative of the sequential decomposition which satisfies the conditions for the two-stage polymerization, that is for the blockcopolymer formation.

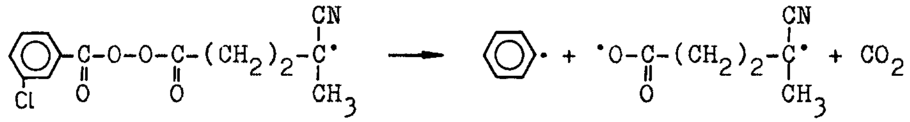
RESULTS AND DISCUSSION

In the first part of the paper the polymerization of acrylamide carried out both thermally and photochemically under the action of the above mentioned initiator is approached.
For initiator photolysis both monochromatic ($\lambda = 366$ nm) and

total spectrum UV radiations were used. In the first case only the quantitative scission of azo groups takes place (SIMIONESCU et al., 1984). The thermal polymerization was carried out in a dioxane solution at different durations, temperatures and initiator concentrations. In some trials an activator (triethylamine) which catalyses the azo group decomposition was also introduced.
The initiator decomposes as follows:



When only thermal decomposition takes place,



Variations in monomer conversion and molecular weight of polyacrylamide initiator function of the mentioned parameters were noticed.

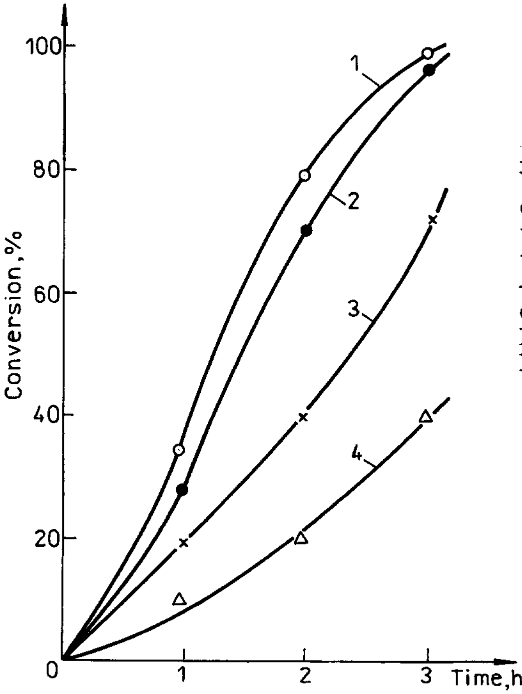


Figure 1.
Variation of acrylamide conversion as a function of time for different initiator concentrations. Solvent - dioxane; Acrylamide concentration - 16,2%; 60°C. 1 - [I] = 1.25%; 2 - [I] = 1.0%; 3 - [I] = 0.50%; 4 - [I] = 0.25%.

The data illustrated in figures 1 - 4 indicate that polymerization of acrylamide with the above mentioned initiator shows the general characteristics of the radical polymerization. The molecular weight decreases with increasing initiator concentra-

tion while the conversion is directly proportional to the amount used and polymerization time.
The initiator decomposition induced by the total spectrum of UV radiations leads to a higher polymerization rate than in the case of monochromatic radiation (λ= 366 nm) (Figures 5,6).

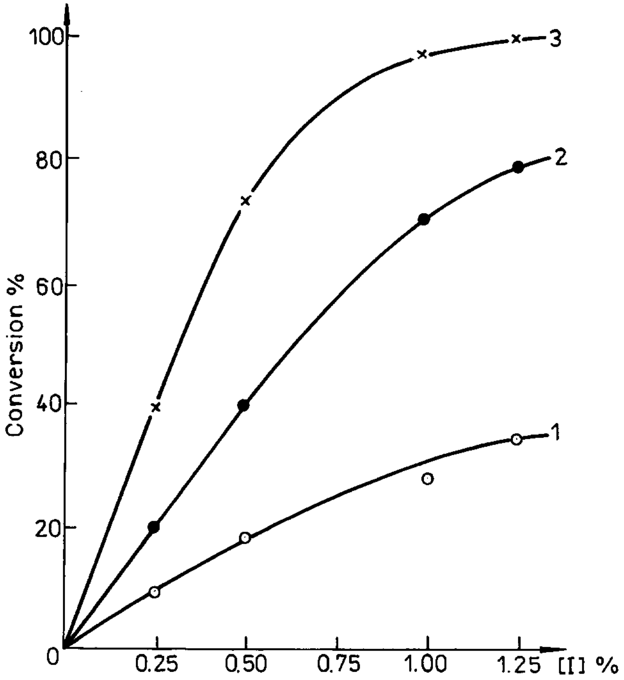


Figure 2.
Variation of acrylamide conversion versus initiator concentration for different polymerization durations.
1 - 1 h; 2 - 2 h;
3 - 3 h.

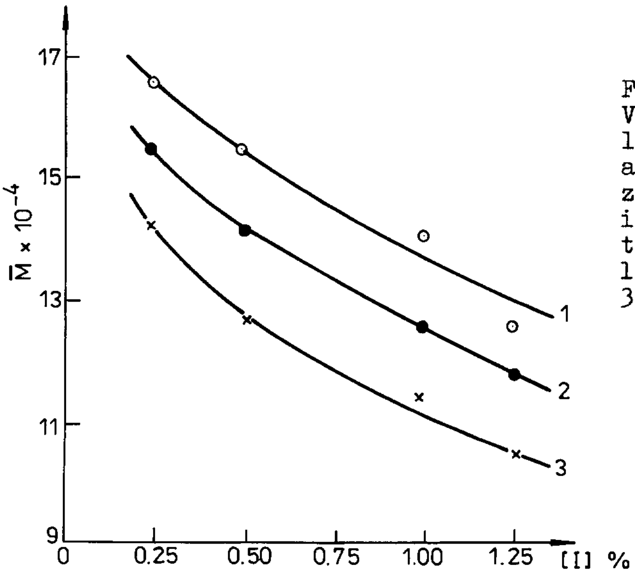


Figure 3.
Variation of molecular weight of polyacrylamide synthesized with different initiator concentrations.
1 - 1 h; 2 - 2 h;
3 - 3 h.

In the first case a much higher number of radicals are generated as a consequence of the simultaneous photolysis of the azo and peroxy groups.

The linear conversion - [I] dependence obtained with monochromatic UV radiations is indicative of a second order polymerization.

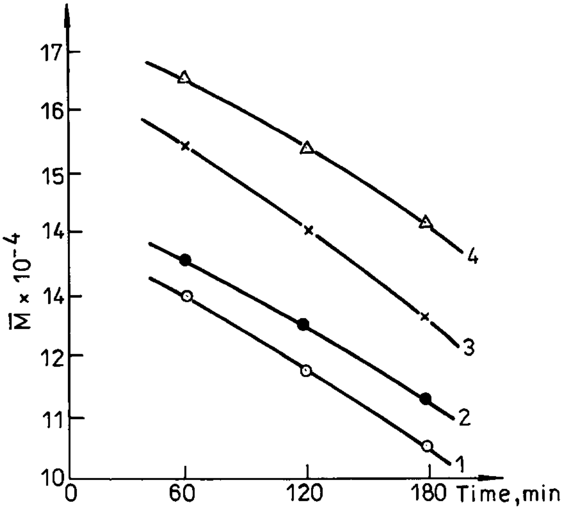


Figure 4.
Variation of molecular weight of polyacrylamide synthesized at different polymerization durations.
1 - [I] = 1.25%; 2 - [I] = 1.00%; 3 - [I] = 0.50%; 4 - [I] = 0.25%.

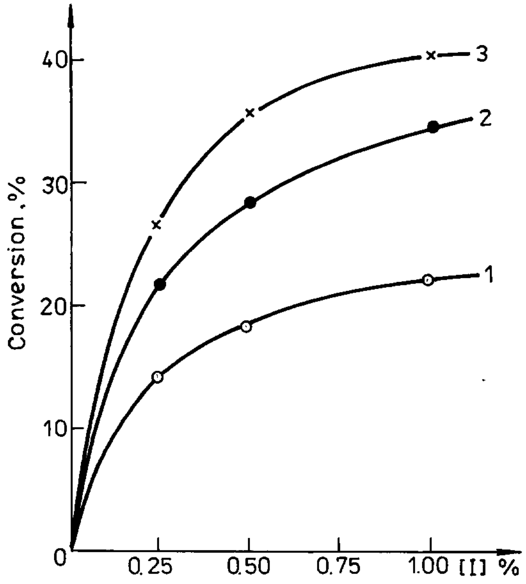


Figure 5.
Variation of acrylamide conversion as a function of initiator concentration for different durations. Total spectrum of UV radiations. Solvent - dioxane; Acrylamide concentration - 19.41%.
1 - 1 h; 2 - 2 h;
3 - 3 h.

A comparison of the molecular weights of the polymers obtained by the two methods indicates those resulting with monochromatic radiation to be higher (Figures 7 - 8).

In order to increase the initiator efficiency triethylamine

(TEA) was introduced in the system in stoechiometrical amount toward the peroxy groups (Table 1). The data in table 1 indicate a negative action of TEA, namely the conversion and molecular weight lowering in time. This phenomenon might be explained by the double effect of TEA as catalyst for peroxy group decomposition and inhibitor of the formed radicals due to the complexation with the nitrogen unpaired electrons. Besides, chain propagation is hindered by TEA inhibiting effect and polymers of molecular weights lower than in the case of thermal polymerization are formed.

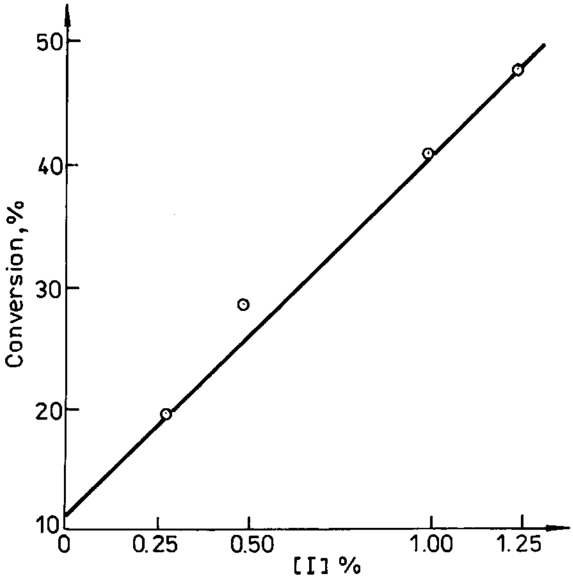


Figure 6.
Variation of acrylamide conversion as a function of initiator concentration. Monochromatic UV radiation (λ= 366 nm). Monomer concentration - 16.2%; Solvent dioxane.

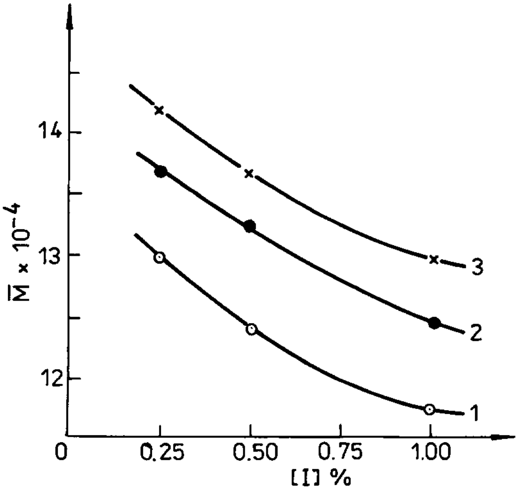


Figure 7.
Variation of molecular weight of the polyacrylamide obtained by initiator photolysis with total UV radiations.
1 - 1 h; 2 - 2 h; 3 - 3 h.

To test the sequential character of the azoperoxidic initiator a series of two-stage polymerizations were carried out. In the first stage the system was maintained under the conditions of

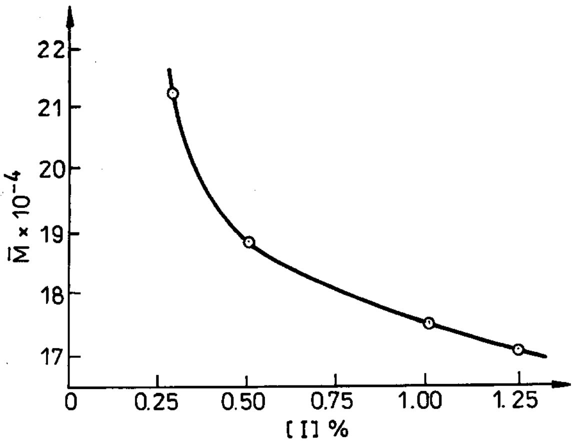


Figure 8.
Variation of molecular weight of the polyacrylamide obtained by initiator photolysis with monochromatic UV radiations. (λ= 366 nm).

Table 1

Polymerization of acrylamide in the presence of initiator and TEA

Time (h)	Conversion (%)	$[\eta]$	$\bar{M}$
4	29.7	1.15	211756
8	49.3	0.87	149404
16	62.8	0.85	145123
32	84.0	0.78	130341
44	99.0	0.74	121216

Temperature = 60°C; Dioxane; [I] = 0.21% (refered to the monomer); TEA = 0.0352 mol/l.

minimum decomposition of the peroxy groups (60°C, 24 h) and maximum decomposition of the azo groups. After a stationary period a room temperature (6 - 8 h) during which all the radicals were deactivated the reaction mixture was heated again for the scission of the peroxy end groups of the polyacrylamide chain. In this way double molecular weights as compared to the one-stage procedure have been obtained (Table 2).

Table 2
Two-stage polymerization of acrylamide with different initiator concentrations

	Temperature (°C)	Time (h)	[I] %	Conversion (%)	$[\eta]$	$\bar{M}$
Stage I	60	2	0.24	-	-	-
	60	2	0.46	-	-	-
	60	2	0.67	-	-	-
Stage II	80	16	-	99.4	2.10	449508
	80	16	-	99.5	2.08	444163
	80	16	-	99.9	2.05	436170

Solvent - dioxane/water 5/25 (v/v).

CONCLUSIONS

The radicalic polymerization of acrylamide was achieved by both thermolysis and photolysis of the 4,4'-azo-bis-(4-cyanovaleryl) -bis-(m-chlorobenzoyl) diperoxide as initiator.
The photolysis with monochromatic UV radiations leads to polymers of maximum peroxy group content, the polymerization being of the second order.
TEA acts as an activator of the peroxy group decomposition and as an inhibitor for the radicals in the system.
The initiator sequential character was tested by the two-stage polymerization of acrylamide when polymers of double molecular weights compared to the one-stage procedure were obtained.

REFERENCES

ANAND,P.S., STAHL,H.G. and HEITZ,W: Makromol. Chem. 183, 1685 (1982)
BILINA,G.S., MATVENTEVA,M.S. and OLIDEKOP,IU.A.: Vysokomol. Soed. 19 555 (1977)
GUNESIN,B.Z. and PIIRMA,J.: J. Appl. Polym. Sci. 26 3103 (1981)
PIIRMA,J. and CHOU,H.LEE-PET: J. Appl. Polym. Sci. 24 2051 (1979)
SHAIKH,A.S., DUMITRIU,S., COMANITA,E and SIMIONESCU,CR.: Polym. Bull. 3 363 (1980)
SIMIONESCU,CR., COMANITA,E., DUMITRIU,S. and MACOVEI,I.: Chem. Zvesti 37 693 (1983)
SIMIONESCU,CR., KIM GYU SIK, COMANITA,E. and DUMITRIU,S.: Angew. Makromol. Chem. in press.
SIMIONESCU,CR., KIM GYU SIK, COMANITA,E. and DUMITRIU,S.: Eur. Polym. J. in press.

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