

## Bifunctional initiators

### IV. Synthesis and characterization of 4,4'-azo-bis-(4-cyanovaleryl)-4-nitrobenzoyl diperoxide

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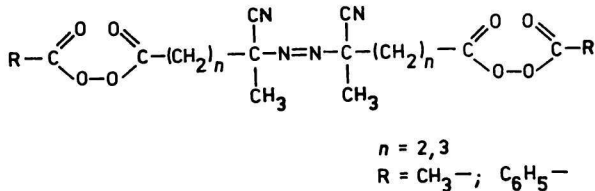
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The paper is concerned with the synthesis and characterization of a new bifunctional initiator — 4,4'-azo-bis(4-cyanovaleryl)-4-nitrobenzoyl diperoxide. The synthesis was performed starting from the acid chloride of the 4,4'-azo-bis(4-cyanovaleric) acid which was condensed with 4-nitroperbenzoic acid. The kinetic study of the thermal decomposition of the initiator yielded the establishment of the decomposition rates, activation energies, and half-life time. The new initiator was used to obtain poly(styrene-*b*-acrylic acid) copolymers.

Работа касается синтеза и характеристики нового бифункционального инициатора, диперекиси 4,4'-азо-бис(4-циановалерил)-4-нитробензоила. Его синтез был осуществлен конденсацией хлорангидрида 4,4'-азо-бис(4-циановалериановой) кислоты с 4-нитробензойной кислотой. Кинетическое изучение термического разложения инициатора было завершено определением скорости разложения, энергии активации и периода полуразложения. Новый инициатор был использован для получения сополимеров полистирол-*b*-акриловой кислоты.

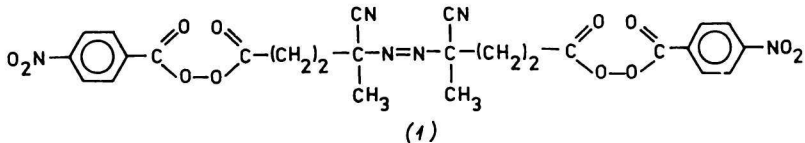
Although the azoperoxide initiators excited a great interest their research as well as the practical applications developed rather slowly. The reason for this might be the difficulties of synthesizing the azoalcanocarboxylic acids which are the principal starting compounds. Besides, the acid chloride can be separated with difficulties as crystalline compound. The research advances are more evident in the azoperester field [1—3] while in the azodiacylperoxide field are rather few.

In previous papers [4, 5] a new type of azodiacylperoxide bifunctional initiators of the general formula given below was reported

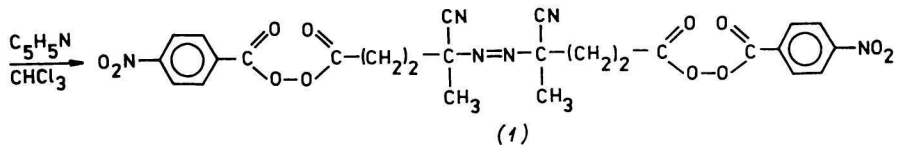
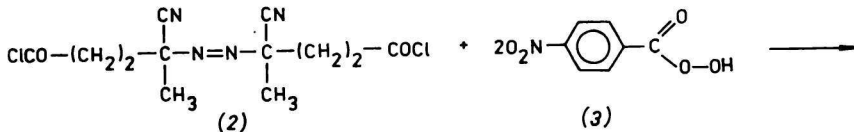


These compounds were found to divide thermally in two stages acting as bifunctional initiators in the polymerization processes [6] yielding block copolymers.

In the present communication the synthesis and study on the properties of a new azodiacylperoxide, namely 4,4'-azo-bis(4-cyanovaleryl)-4-nitrobenzoyl diperoxide of the following structure are reported



The product is obtained by condensation of 4,4'-azo-bis(4-cyanovaleryl chloride) with 4-nitroperbenzoic acid in the presence of pyridine in chloroform medium.



The acid chloride was obtained by treating the 4,4'-azo-bis(4-cyanovaleric) acid with  $\text{PCl}_5$ . The Smith method [7] was modified by us as given in previous papers [4] and now improved, which resulted in obtaining a white crystalline chloride in a higher yield.

The condensation reaction of 4,4'-azo-bis(4-cyanovaleryl chloride) with 4-nitroperbenzoic acid was performed in homogeneous chloroform and pyridine medium for hydrogen chloride bonding instead of aqueous KOH. The reaction

The classical kinetic model of free radical polymerization assumes that the reactivities of the growing chains are independent of their lengths and that the termination rate constant is also independent of the chain length. However, both theoretical and experimental work in the last years has shown that in diffusion-controlled reactions, the termination rate constant is a function of the chain length [12—14].

In the case of plasma-induced polymerization, the initiation takes place at the very beginning of the reaction and the initiation efficiency is small, so that a small number of radicals become growing macroradicals. The transfer constants to monomer and polymer (copolymer) have reduced values at room temperature and, in time, part of the macroradicals are immobilized in the reaction system due to the important viscosity of the medium, so that recombination or disproportionation reactions are quite impossible. The ultralong chains remain active in time, becoming “living” macroradicals.

The experiments performed to prove the existence of “living” macroradicals and to use them as “macromolecular initiators” are shown in Scheme 1. In all three cases, the polymer formed in the first stage was kept at room temperature for long periods of time and then a new amount of monomer was added; the whole process took place in vacuum.

These results are not the only ones existing on “living” macroradicals. Different other papers considered “living” radical polymerization and copolymerization [15], but their formation and acting in this case is the most interesting one.

Certainly, the post-polymerization rate has to decrease in time, but for very long post-polymerization periods — as a result of either the annihilation, by chemical transformation, of the macroradicals, or of their “immurement” in the formed polymer by physical deactivation.

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