Polymer Bulletin 16, 235–241 (1986)

Polymer Bulletin

Azo peroxide initiators

Synthesis and characterization of O-[4-(t-butylazo)-4-cyanovaleryl]-O'-acetyl peroxide

C. I. Simionescu*, Eugenia Comăniță, Mariana Păstrăvanu, and I. Druță

Department of Organic and Macromolecular Chemistry, Polytechnic Institute,
RO-6600 Jassy, Romania

SUMMARY

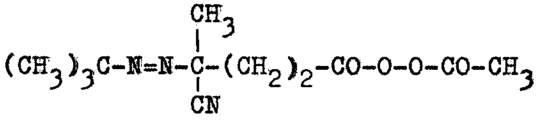
Azo diacyl peroxide compounds have been successfully used as sequential bifunctional initiators, in reactions of radicalic polymerization of vinyl monomers, for block copolymer obtaining. Resuming previous investigations, the O-[4-(t-butylazo)-4-cyanovaleryl]-O'-acetyl-peroxide has been synthesized; this is a new azo diacyl peroxide compound, obtained either by the direct condensation of the 4-(t-butylazo)-4-cyanovaleric acid (the BACV acid) with peracetic acid - under the dehydrating action of the dicyclohexylcarbodiimide - or from the chloride of the respective acid by treatment with peracetic acid in the presence of pyridine. The initiator structure is confirmed by the characteristics evidenced by IR and ^{1}H-NMR, as well as by the ^{13}C-NMR spectra. The synthesized product may be kept, in cold conditions, for a long time; nevertheless, by contact with a base it manifests the tendency of changing itself into a symmetrical azo diacyl peroxide.

INTRODUCTION

Bi- and polyfunctional initiators with sequential decomposition have aroused interest in the radical polymerization of vinyl monomers, aiming at the obtainment of "active polymers" which, being breakable at the labile groups, left intact, may play - in another polymerization stage - the role of macromolecular initiators (SHEPPARD and MACLEAY, 1970; MACLEAY and SHEPPARD, 1976). The two - step polymerization permits a quite simple and direct preparation of block copolymers, which can be commercially used as elastomers, fibers, adhesives, thermoplastics, elastoplastics, surfactants, etc. (PIIRMA et al., 1979). Numerous and various initiators of the polyperoxide, polyazo and azo peroxide compound classes are already known. The last ones in this series are referred in the present paper which, resuming subsequent investigations (SIMIONESCU et al., 1982, 1983, 1984; SHAIKH et al., 1980, 1981; DUMITRIU et al., 1983) deals with the synthesis of an azo diacyl peroxide initiator of the form:

---

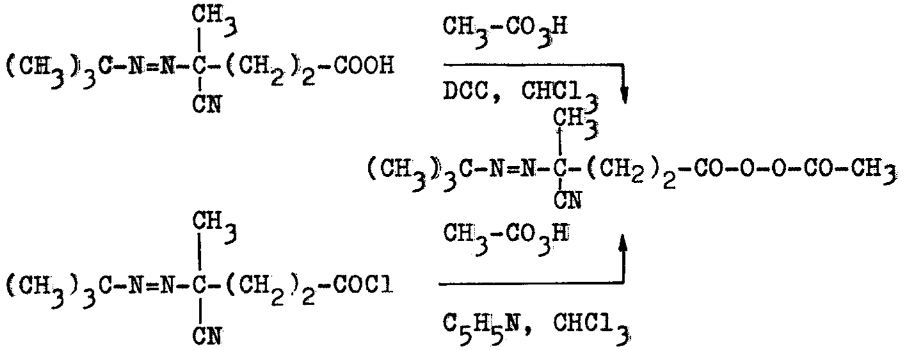
* To whom offprint requests should be sent



$$(CH_3)_3C\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\text{-}CO\text{-}O\text{-}O\text{-}CO\text{-}CH_3$$

RESULTS AND DISCUSSION

As azoacylating component, the 4-(t-butylazo)-4-cyanovaleric acid (BACV acid) was used, which is accesible by the reaction between the t-butylhydrazine chlorhydrate, levulinic acid and natrium cyanide (SHEPPARD and MACLEAY, 1977). Condensation to hydrazone, hydrocyanuration and then, oxidation with bromine occur without the separation of intermediates, finally resulting the cyanazo acid with a yield of 72%. The peroxy function, the second labile group, has been introduced by reaction with peracetic acid.
The literature in the field makes mention of some azo peresters (SHEPPARD and MACLEAY, 1976; MACLEAY and SHEPPARD, 1977) and a symmetrical azo diacyl peroxide, obtained with the same azoacid, which was peroxidated as acid chloride, with alkyl hydroperoxide and hydrogen peroxide, respectively (SHEPPARD et al., 1969).
The O-[4-(t-butylazo)-4-cyanovaleryl]-O'-acetyl peroxide synthesis was performed by two variants. The former consists of the direct condensation of the BACV acid with peracetic acid under the dehydrating action of the dicyclohexylcarbodiimide (DCC).



$$(CH_3)_3C\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\text{-}COOH \xrightarrow[DCC,\ CHCl_3]{CH_3\text{-}CO_3H} (CH_3)_3C\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\text{-}CO\text{-}O\text{-}O\text{-}CO\text{-}CH_3$$

$$(CH_3)_3C\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\text{-}COCl \xrightarrow[C_5H_5N,\ CHCl_3]{CH_3\text{-}CO_3H} (CH_3)_3C\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\text{-}CO\text{-}O\text{-}O\text{-}CO\text{-}CH_3$$

The reaction was conducted in an anhydrous chloroform medium, in which the dicyclohexylurea formed by DCC hydration, is almost insoluble and thus separable of the initiator left in the solution.
The latter synthesis used the BACV acid chloride, which reacts with the peracetic acid in the presence of pyridine, in anhydrous chloroform. The acid chloride was obtained by treating BACV acid with PCl_5, in cold conditions(5°C), in anhydrous benzene. After washing with water and 5% natrium carbonate solution - previously cooled - the chloroformic solution of initiator is distilled in vacuum, for the removal of solvent, the last operation being performed at a temperature under 35°C, in order to avoid the decomposition of the thermolabile groups. The resulting crystalline com-

pound has a melting point of 39-40°C which, by purification (dissolving in CCl_4 or ethyl ether and hexane precipitation) raises only up to 43°C (with decomposition). The product is soluble in almost all common organic solvents: methanol, ethanol, acetone, ethyl ether, benzene, halogenated derivatives.

The azo peroxide structure is confirmed by spectroscopic measurements. Thus, the IR spectrum contains the ν_{CO} band, characteristic to acyl peroxides, as a doublet, at 1780 and 1810 cm^{-1}, as well as the absorptions of the groups ν_{CN} (2235 cm^{-1}), $\nu_{N=N}$(980 cm^{-1}), ν_{CH}(2870, 2930, 2980 cm^{-1}) etc. The ^1H-NMR spectrum ($CDCl_3$) exhibits chemical shifts at the following δ values (ppm): 1.27 ($3CH_3$), 1.6 (CH_3-$\overset{|}{\underset{|}{C}}$-CN), 2.18 ($CH_3$-CO), 2.49 (2 CH_2) (Figure 1). An evidence of the accepted structure is offered too by the ^{13}C-NMR spectrum (Puls-Fourier Transform), showing the following chemical shifts (δppm): 167.59 and 165.17 (2 CO), 118.54 (CN), 70.54 and 68.70 (2 $>C<$), 32.92 and 25.23 (2 CH_2), 26.52 (3 CH_3), 23.68 (CH_3-$\overset{|}{\underset{|}{C}}$-), 16.45 ($CH_3$-CO) (Figure 2).

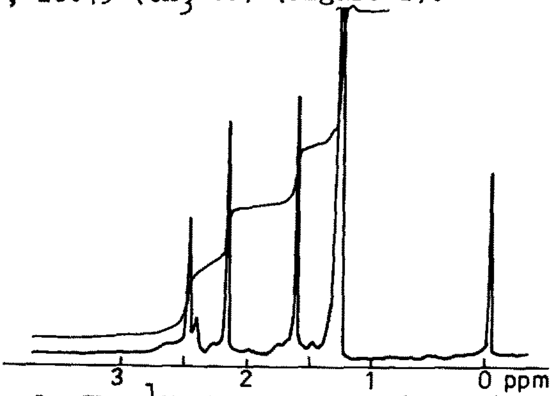


Fig. 1 The ^1H-NMR spectrum ($CDCl_3$) of azo peroxide initiator

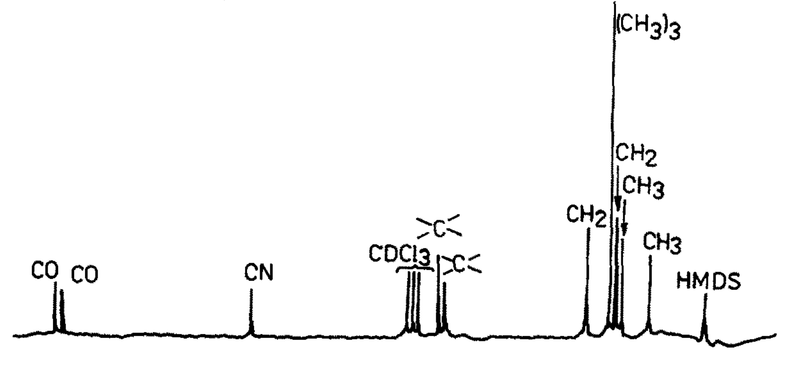
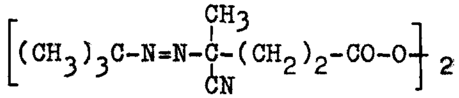


Fig. 2 The ^{13}C-NMR spectrum ($CDCl_3$) of azo peroxide initiator

In certain conditions, the azo peroxide proves unstable. A specific and - at the same time - surprising behaviour is to be observed during its treatment, in a finely pulverized form, with a dilluted solution of sodium carbonate. Such a operation was employed for the removal from the raw product (m.p. 39-40°C) of the acid traces (BACV acid). After a first treatment with alkaline solution, the melting point suddenly raises to 67 - 69°C and on repeating the operation, to 84 - 85 °C. A similar behaviour is to be observed with the pure product. Simultaneously, data of elementary analysis are being modified (the percentage carbon content increases from 53.61 to 56.85 %). Structural investigations of the compound possessing a high melting point indicate the formation of a symmetrical azo peroxide having the following form:



$$\left[(CH_3)_3C\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\text{-}CO\text{-}O\right]_2$$

The ^{1}H-NMR spectrum ($CDCl_3$) evidences δ values (ppm) of the chemical shifts at 1.27 ($3CH_3$), 1.61 (2 CH_3-C-CN), 2.51 (2 CH_2). The ^{13}C-NMR spectrum (Puls Fourier Transform) confirms the symmetrical structure, through the following chemical shifts (δ ppm): 167.49 (2 CO), 118.42 (2 CN), 70.47 and 68.62 (4 >C<), 32.83 and 25.13 (4 CH_2), 26.49 (6 CH_3), 23.60 (2 CH_3-C-) (Figure 3).

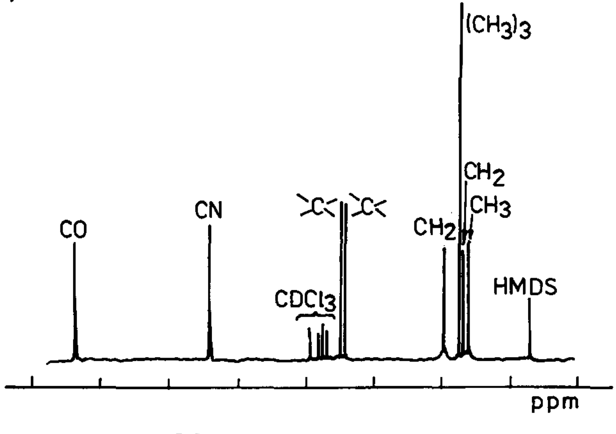
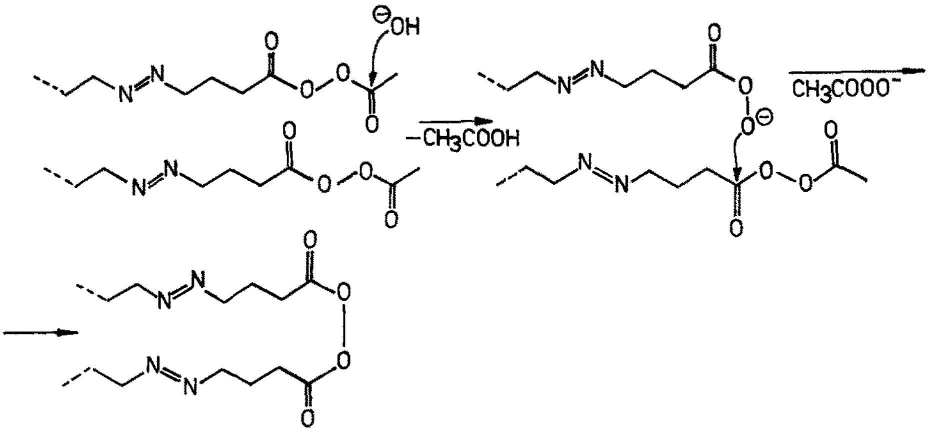


Fig. 3 The ^{13}C-NMR spectrum ($CDCl_3$) of bis-[4-(t-butylazo)-4-cyanovaleryl]-peroxide

This azo peroxide has been also prepared, but in a different manner - that is, from BACV acid chloride and hydrogen peroxide (SHEPPARD et al., 1969).
The transformation of the unsymmetrical azo peroxide in a symmetrical product, by washing with an aqueous solution of Na_2CO_3, could be due to certain interphase reactions, assuming a packed arrangement, towards the inside of the particles of the hydrophobic residue (showing a low polarity) as well as the orientation towards the aqueous solution of

the acetyl peroxy residue (having a higher polarity). This molecular arrangement promotes the basic attack to the CO group from the acetyl residue, followed by the breaking of the corresponding C-O link, resulting in the formation of acetic acid (sodium salt) and the anion of the BACV acid.



This will nucleophilically attack the carbonyl group from a neighbouring molecule, accompanied by the release of the peracetic anion. The transformation from the unsymmetrical to the symmetrical azo diacyl peroxide is energetically favourable, due to the high thermodynamic stability of the latter compound.

EXPERIMENTAL

BACV acid chloride

In a 250 ml flask with three necks, equipped with condensator and mechanical stirrer, 5 g (0.024 mol) of BACV acid and 80 ml of anhydrous benzene are introduced. The mixture is cooled at 5-6°C, then it is treated, for another half an hour, with 6.62 g (0.032 mol) PCl_5 while maintaining the temperature between 0-5°C. Stirring is continued for other 2-3 hours, at the indicated temperature, then the liquid - yet containing unsoluble substances - is left overnight at room temperature. Stirring is resumed for other 30 minutes, whether the solid haven't completely disappeared. The solution is filtered off (avoiding the atmospheric contact) and distilled in vacuum, on a water bath, at maximum 35 - 40°C, for removing benzene and the phosphor oxychloride. The residue obtained is a viscous liquid, which, up to its utilization, has to be kept in a cool, dry place.

O- [4-(t-butylazo)-4-cyanovaleryl] -O'-acetyl peroxide

a) The DCC method

In a three necked flask, equipped with stirrer, condensator and dropping funnel, 2.06 g (0,01 mol) DCC and 30 ml dry chloroform are introduced. Over the obtained suspension, a solution of 2.11 g (0.01 mol) BACV acid and 20 ml chloroform, mixed with 9 ml chloroformic solution of peracetic acid (0.76 g; 0.01 mol) is dropped. The liquid is stirred for 48 h, at room temperature, when a more and more abundant separation of the dicyclohexylurea (DCU) is observed. After its filtration, the solution is concentrated to 1/3 of the initial volume, then it is left in the refrigerator for a more complete separation of DCU. The filtrate is washed in a funnel with water, a solution of 5% Na_2CO_3 and again with water, all these having been previously cooled. The chloroformic layer is dried on $MgSO_4$ and is distilled in vacuum. The residue obtained, a yellow, viscous oil is crystallized by being kept in a cool place. The product is purified by dissolution in ethyl ether, filtration of the DCU traces and adding of n-hexane up to becoming opalescent.

b) <u>The acid chloride method</u>

Over 23 ml chloroformic solution of peracetic acid (1.86 g; 0.025 mol) cooled at -5°C, 1.97 g (0.025 mol) pyridine are dropped, under stirring. At the same temperature, there is added, in about 25 minutes, the acid chloride obtained in a previous stage, solved in 20 ml chloroform. Stirring is continued for 5 h at 0-5°C, then the mixture is left overnight, at room temperature. The chloroformic solution is washed with 25 ml water (twice), 25 ml of 5% Na_2CO_3 solution and again with 25 ml of water, the liquids being previously cooled. The organic layer is dried on anhydrous natrium sulphate and is subjected to distillation in vacuum up to the complete evaporation of chloroform; 4.5 g of raw product are thus obtained, with a m.p. of 39-40°C (yield 70.64 %) which is afterwards purified by solving it in some CCl_4 (or ethyl ether), n-hexane addition - up to opalescence (with exceding a certain limit, an oily product is being separed) and left for crystallization in the freezer.

The authors thank Professor M. Schulz of the Technische Hochschule "Carl Schorlemmer", Leuna - Merseburg, GDR, for the ^{13}C-NMR spectra recorded.

REFERENCES

C.S. SHEPPARD and R.E. MACLEAY, BRD 1.940.473, 19.02.1970; CA: 72, 90983m (1970)
R.E. MACLEAY and C.S. SHEPPARD, US. 3.987.024, 19.10.1976; Ref. Zh. 13 (II) 13.H. 297 P (1977)
IRJA PIIRMA and LEE PEI H. CHOU, J. Appl. Polym. Sci., 24, 2051 (1979)
C.I. SIMIONESCU, E. COMANITA, S. DUMITRIU, A. PETROVICI and A. S. SHAIKH, Revista de Chimie, 33, 423 (1982)
C. I. SIMIONESCU, E. COMANITA, S. DUMITRIU and I. MACOVEI, Chem. Zvesti, 37, 693 (1983)
C.I. SIMIONESCU, KIM GYU SIK, E. COMANITA and S. DUMITRIU, Eur. Polym. J., 20, 467 (1984)
A.S. SHAIKH, S. DUMITRIU, E. COMANITA and C.I. SIMIONESCU, Polym. Bull., 3, 366 (1980)
A.S. SHAIKH, E. COMANITA, S. DUMITRIU and C.I. SIMIONESCU, Die Angew. Makromol. Chemie, 100, 147 (1981)
S. DUMITRIU, A.S. SHAIKH, E. COMANITA and C.I. SIMIONESCU,

Eur. Polym. J., 19 263 (1983)
C.S. SHEPPARD and R.E. MACLEAY, US. Pat. 4.045.427, 30.08. 1977; CA: 87, 168628f (1977)
C.S. SHEPPARD and R.E. MACLEAY, US. Pat. 3.956.269, 11.05. 1976; Ref. Zh. 1 (II) 1.H. 201 P (1977)
R.E. MACLEAY and C.S. SHEPPARD, US. Pat. 4.001.207, 04.01. 1977; Ref. Zh. 17, 17479 P (1977)
C.S. SHEPPARD, R.A. BAFFORD and R.E. MACLEAY, BRD Pat. 1.905.915, 11.09.1969; CA: 72, 13201c (1970)

Accepted September 5, 1986 *C*