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ORIGINAL PAPER

Synthesis and thermal properties of azo-peroxyesters

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Abstract New azo-perester derivatives of *tert*-butyl and *tert*-amyl hydroperoxides were obtained in reactions of azo acid chlorides with hydroperoxides in the presence of an inorganic base. Obtained azo-peresters possess two kinds of the labile functional groups: the azo group and also the perester group. The data from DSC experiments indicate that in the case of azo-perester derivatives of *tert*-amyl hydroperoxide, the perester group decomposes at a somewhat lower temperature than in the case of *tert*-butyl derivatives, whereas azo groups decompose at somewhat higher temperature in the case of derivatives with *tert*-amyl substituent.

Keywords Diazo compounds · Calorimerty · Bifunctional initiators · NMR spectroscopy · Thermal decomposition

Introduction

Since 1909 when *Fritz Hofmann* from the firm Bayer got his first patent concerning the radical polymerization of isoprene, processes of radical polymerization and copolymerization have played an important role in modern chemistry. The fact that the process of radical polymerization is still of interest may be proved by the considerable number of publications and patents dealing with this range of knowledge issued in recent years. Radical polymerizations are constantly under development thanks to the proper choice of conditions of running these processes and also to the modification of the applied additives, and development of novel initiators, including multifunctional ones. Interesting results have been achieved due to the application of the so-called bi- and polyfunctional initiators [1–5].

In comparison with monofunctional initiators, bifunctional initiators display a number of advantages, namely that with the increasing concentration of the initiator, polymer with a higher molar mass is formed, which also displays a higher rate of initiation [6] if compared with the traditional applied initiators.

As far as their structure is concerned, bi- and polyfunctional initiators are characterized by the fact that they contain at least two or even more labile links, identical or various ones. Therefore, these initiators may be generally divided into bi- and polyperoxides, bi- and polyazo compounds, and azo-peroxides.

Chemical compounds can play the role of a bi- or polyfunctional initiator when the active groups contained in the molecule display a differing thermal or photochemical stability and are connected with another carbon atom in the molecule.

Azo-peroxy compounds may be generally divided into three main groups: azo-peresters, azo-diacyl peroxides, and azo-dialkyl peroxides.

Generally, compounds of this type are most often obtained by means of two different methods [1–4, 7–11]: (1) by joining aliphatic azo compounds with peroxy compounds applying such reactions as: esterification, etherification,

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carbonates or amides formation; (2) by oxidizing aliphatic azo compounds with hydrogen peroxide or sodium peroxide.

The literature provides information about the production of several azo-peresters and investigations concerning the initiating ability of these compounds [7, 8, 12, 13]. All the investigated and described compounds were based on known azo derivatives [8, 12] and *tert*-butyl hydroperoxide. Azo-peresters with *tert*-amyl substituent have not been described so far.

The thermal and photochemical decomposition of azo and peroxy bonds in azo-peroxy compounds has been described in detail with respect to the azo-diacyl peroxides [10, 11, 13, 14]. In the case of other groups, this problem has not been profoundly investigated yet. None of the azo-peroxy compounds described in the literature was examined with the DSC method.

Results and discussion

The investigated initiators contain in their molecule azo group and two peresters groups that display a varying thermal stability, and they may decompose into radicals at two different temperatures.

All the presented azo-peresters were the results of the reactions illustrated in Scheme 1.

Besides the derivatives of 4,4′-azobis-(4-cyanopentanoic) acid (**2a**), also *tert*-butyl and *tert*-amyl azo-peresters of the homologous of this acid with azo function were obtained, with a varying number of methylene groups separating both these groups (from 2 to 4).

The reaction of respective 5,5′-azobis-(5-cyanohexanoic) acid (**2b**) and 6,6′-azobis-(6-cyanoheptanoic) acid (**2c**) was run in compliance with the procedure described by Shaikh [15], though somewhat modified in that the duration of the first stage of the reaction, i.e., the formation of hydrazone, was prolonged from 24 to 36 h, thanks to which the efficiency of the reaction could in the case of 5,5′-azobis-(5-cyanohexanoic) acid (**2b**) be increased from 50 to 75%. The 6,6′-azobis-(6-cyanoheptanoic) acid (**2c**) has not been dealt with in the literature so far.

The synthesis of the 5,5′-azobis-(5-cyanohexanoic) acid chloride (**3b**) and 6,6′-azobis-(6-cyanoheptanoic) acid chloride (**3c**) was run in compliance with the procedure suggested by Shaikh [15].

The preliminary results obtained in the course of investigations concerning the di-*tert*-butyl-4,4′-azobis-(4-cyanoperoxypentanoate) (**4a**) have made it possible to determinate the conditions of the synthesis of azo-peresters, which permit obtaining these compounds with a rather good yield and purity: the molar ratio of the hydroperoxide to the chloride of azo-acid amounts to 5:1; the applied base is a 40% NaOH solution. Moreover, due to the solubility of the reagents, the synthesis must be carried out in chlorinated solvent.

All compounds were prepared with moderate yields, but the derivates of *tert*-amyl hydroperoxide (**5a–c**) were obtained with lower yields than the derivates of *tert*–butyl hydroperoxide (**4a–c**).

An extension of the length of the carbon chain between both these groups resulted in an increased yield of the obtained compounds.

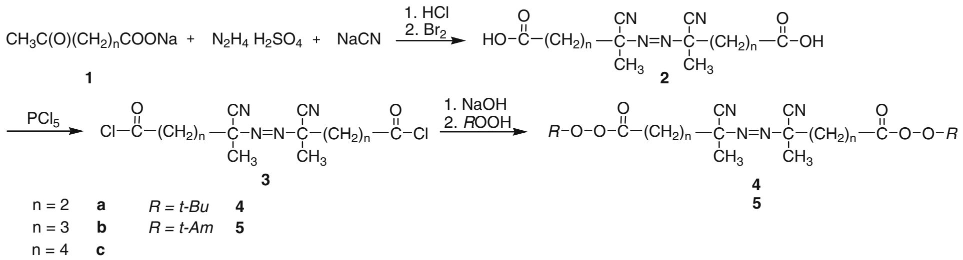
The obtained azo-peresters were characterized by means of spectroscopic methods: ^{1}H NMR, ^{13}C NMR, IR, and elementary analysis.

The thermal decomposition of the obtained azo-peresters was studied by the DSC method; the results of selected examples are presented in the diagrams below: for *tert*-butyl derivative (Fig. 1) and *tert*-amyl derivative (Fig. 2) of 4,4′-azobis-(4-cyanopentanoic) acid (**2a**).

The diagrams indicate the process of melting of the compound as well as two peaks resulting from the exothermal decomposition of the azo and the perester groups. In all these cases, the first peak displays the exothermal decomposition of the azo group, whereas the second peak shows the decomposition of the perester group.

In order to confirm that the first peak concerns the decomposition of the azo group and the second one the perester group, tests have been carried out consisting of the heating of azo-peresters (**4a** and **5b**) with 1% addition of cobalt stearate. It has been already demonstrated that the addition of a transition metal salt induces the decomposition of the peroxy bonds [16], without considerably affecting the decomposition of the azo bonds. In order to check this influence on the azo group, analogical tests have been carried out with 4,4′-azobis-(4-cyanopentanoic) acid

Scheme 1



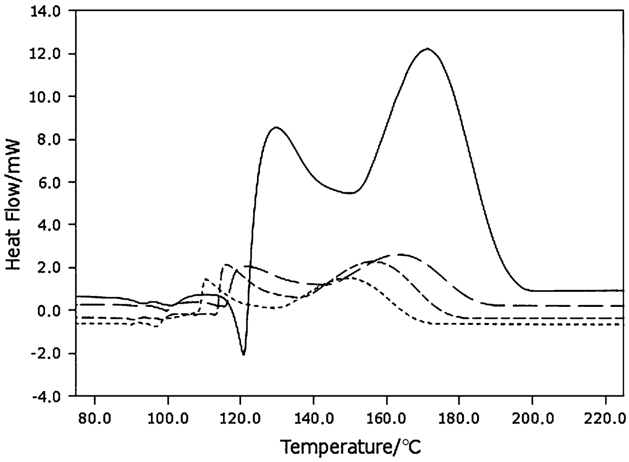


Fig. 1 DSC curves of the samples di-*tert*-butyl-4,4′-azobis-(4-cyanoperoxypentanoate) (**4a**) at different heating rates: *solid line* 20°/min; *dotted line* 10°/min; *dotted dashed line* 5°/min; *dashed line* 2.5°/min

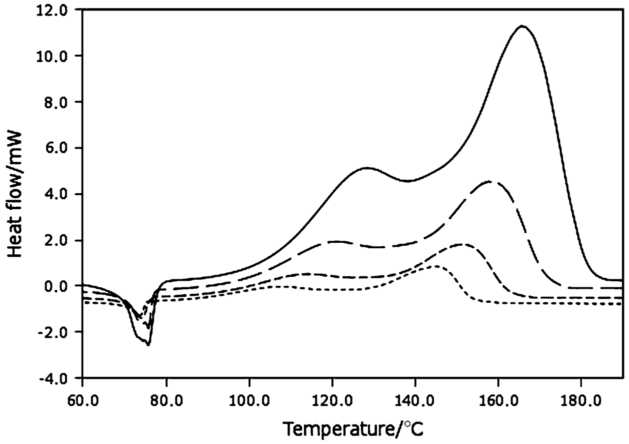


Fig. 2 DSC curves of the samples di-*tert*-amyl-4,4′-azobis-(4-cyanoperoxypentanoate) (**5a**) at different heating rates: *solid line* 20°/min; *dotted line* 10°/min; *dottted dashed line* 5°/min; *dashed line* 2.5°/min

Table 1 Temperatures at the maximum of the exotherms (T_p) of azo-peresters and azo compounds with 1% mass amount of cobalt stearate (constant heating rate 10 °C min^{-1})

	Temperature/°C			
	With addition of salt		Without addition of salt	
Compound	–N=N–	–O–O–	–N=N–	–O–O–
2a	131.7	–	133.8	–
ACHN	144.1	–	145.1	–
4a	120.8[a]	129.2	118.7	163.8
5b	120.4[a]	132.2	122.7	156.4

[a] Peak present at DSC grams under main (second) peak

Table 2 Temperatures at the maximum of the exotherms (T_p) of azo-peresters under various heating rates

Azo-perester derivatives of *tert*-butyl hydroperoxide

	Temperature/°C					
	4a		**4b**		**4c**	
β/°C min^{-1}	–N=N–	–O–O–	–N=N–	–O–O–	–N=N–	–O–O–
1	103.3	142.6	101.0	138.2	104.8	138.0
2.5	108.2	151.0	107.1	147.2	108.6	146.6
5	113.0	157.2	112.7	153.1	114.5	153.2
10	118.7	163.8	120.0	159.8	121.0	159.9
20	126.2	170.9	126.1	165.9	127.5	164.9

Azo-perester derivatives of *tert*-amyl hydroperoxide

	Temperature/°C					
	5a		**5b**		**5c**	
β/°C min^{-1}	–N=N–	–O–O–	–N=N–	–O–O–	–N=N–	–O–O–
1	99.8	136.2	94.6	128.7	100.9	134.5
2.5	107.4	144.7	109.3	143.1	108.8	143.0
5	114.1	151.5	114.9	149.1	116.1	149.6
10	120.2	158.7	122.7	156.4	122.7	156.8
20	127.7	165.5	129.2	163.0	129.8	163.4

(**2a**) and α,α′-azobis-(1-cyanocyclohexane) (*ACHN*). The results of these experiments are presented in Table 1.

The obtained data indicate that the addition of cobalt salt does not influence the decomposition of the azo groups in the investigated compounds; the maximum temperature of decomposition as well as the shape of the decomposition peaks do not change in the case of an azo compounds, nor in the case of azo-peresters.

If cobalt salt admixtured, however, the temperature range of decomposition of the perester group changes in azo-peresters. These values are shifted towards lower temperature values by about 25 °C, in results of which the peak of the exothermal decomposition of the azo group merges with the peak displaying the decomposition of the perester functional group.

The progress of the decomposition of *tert*-butyl and *tert*-amyl derivatives is analogous within their homological series. The data concerning the maximum temperature values of the peaks displaying the exothermal decomposition of the remaining azo-peresters are gathered in Table 2.

The data presented in Table 2 indicate that in the case of azo-peresters derivatives of *tert*-amyl hydroperoxide, the perester group decomposes at a somewhat lower temperature than in the case of *tert*-butyl derivatives, whereas azo groups decompose at somewhat higher temperature in the case of derivatives with *tert*-amyl substituent.

Experiment

Tert-butyl hydroperoxide (Merck) was extracted with hexane, *tert*-amyl hydroperoxide (Pergan), and PCl_5 (Merck).

Methylene chloride and benzene were dried over molecular sieves: hydrazine sulphate, sodium cyanide, and 4,4′-azobis-(4-cyanopentanoic) acid (**2a**) (Fluka).

4,4′-Azobis-(4-cyanopentanoic) acid chloride (**3a**) was prepared by Hazer [5] procedure. 5-Oxohexanoic acid (**1b**) was synthesized as described by Bates [17], and 6-oxoheptanoic acid (**1c**) was synthesized as described by Schaeffer [18].

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity Inova-300 spectrometer using TMS as an internal standard. IR spectra were recorded on a Zeiss Specord M 80 spectrometer. The results of elemental analyses agreed favorably with the calculated values.

The thermal characteristics of the investigated materials were obtained using the DSC 2010 TA instrument at heating rates of: 1, 2.5, 5, 10, and 20 °C min^{-1} within the temperature range from −80 to +200 °C. The temperature was calibrated with indium and gallium standards over the whole explored temperature range.

Preparation of carboxylic acids with azo function; general procedure

To a slurry of hydrazine sulphate (0.12 mol) in water, a solution of (0.24 mol) sodium cyanide in water was added slowly at room temperature under very intensive stirring. The solution became clear after 10 min, and stirring was continued for another 20 min. After this, a solution of (0.24 mol) 5-oxohexanoic (**1b**) or 6-oxoheptanoic acid (**1c**) neutralized with sodium carbonate in water was added. The mixture was stirred next for 8 h and left for a further 36 h. Then the mixture was cooled down to 0 °C and carefully acidified with concentrated HCl, and stirred rapidly. To the acidified mixture, bromide was introduced dropwise to excess and stirred for another 1 h. The suspension was poured into ice and stirred until the ice melted. The separated crude product was dissolved in sodium carbonate solution, then precipitated with concentrated HCl, and again filtered. The fine product was dried under a vacuum to a constant weight.

5,5′-Azobis-(5-cyanohexanoic) acid (**2b**; $C_{14}H_{20}N_4O_4$)
Yield 75%; m.p.: 105–107 °C; Ref. [15] m.p.: 115–117 °C; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 8.32 (s, 2H, O*H*), 2.38–2.31 (m, 4H, C*H*$_2$CO), 2.18–2.13 (m, 2H, C*H*$_2$), 2.02–1.92 (m, 2H, C*H*$_2$), 1.73–1.63 (m, 2H, C*H*$_2$), 1.68 (s, 6H, C*H*$_3$), 1.53–1.49 (m, 2H, C*H*$_2$) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 178.49 (*C*O), 118.09 (*C*N), 72.86 (*C*(CN)), 37.40 (*C*H$_2$CO), 33.24 (*C*H$_2$C(CN)), 24.44 (*C*H$_3$C(CN)), 19.73 (*C*H$_2$CH$_2$CO) ppm; IR (CH_3CN): $\bar{\nu}$ = 3600–3160, 2320, 1720, 1460, 1320 cm^{-1}.

6,6′-Azobis-(6-cyanoheptanoic) acid (**2c**; $C_{16}H_{24}N_4O_4$)
Yield 78%; m.p.: 105–107 °C; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 8.80 (s, 2H, O*H*), 2.48–2.30 (m, 4H, C*H*$_2$CO), 2.24–2.14 (m, 2H, C*H*$_2$), 2.05–1.95 (m, 2H, C*H*$_2$), 1.76–1.66 (m, 4H, C*H*$_2$), 1.70 (s, 6H, C*H*$_3$), 1.60–1.48 (m, 2H, C*H*$_2$), 1.39–1.27 (m, 2H, C*H*$_2$) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 179.52 (*C*O); 118.04 (*C*N), 72.78 (*C*(CN)), 37.64 (*C*H$_2$CO), 33.64 (*C*H$_2$C(CN)), 24.21 (*C*H$_2$CH$_2$CO), 24.13 (*C*H$_3$C(CN)), 23.85 (*C*H$_2$CH$_2$C(CN)) ppm; IR (CH_3CN): $\bar{\nu}$ = 3600–3150, 2320, 1710, 1440, 1310 cm^{-1}.

Preparation of acid chlorides; general procedure

A suspension of (0.03 mol) 5,5′-azobis-(5-cyanohexanoic) acid (**2b**) or 6,6′-azobis-(6-cyanoheptanoic) (**2c**) in benzene was cooled down to 0 °C, and (0.09 mol) PCl_5 was slowly added for 15 min. Rapid stirring was continued for 2 h at 0 °C. The resulting mixture was filtered (the remaining azo acid was removed). The solution was stripped off under a vacuum using a rotary evaporator at room temperature. The resulting oil was placed in a freezer. After 12 h, the recrystallized solid was filtered and washed in a solution of 1:1 Et_2O/CH_3Cl and dried in a vacuum exsiccator.

5,5′-Azobis-(5-cyanohexanoic) acid chloride
(**3b;** $C_{14}H_{18}N_4Cl_2O_2$)
Yield: 51%; m.p.: 87–89 °C; Ref. [15]: m.p.: 88–89 °C; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 3.02–2.97 (*t, J* = 6.9 Hz, 4H, C*H*$_2$CO), 2.26–2.16 (m, 2H, C*H*$_2$), 2.14–2.04 (m, 2H, C*H*$_2$), 1.98–1.84 (m, 2H, C*H*$_2$), 1.73 (s, 6H, C*H*$_3$), 1.75–1.62 (m, 2H, C*H*$_2$) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 173.00 (*C*OCl), 117.54 (*C*N), 72.17 (*C*(CN)), 45.98 (*C*H$_2$CO), 36.56 (*C*H$_2$C(CN)), 24.01 (*C*H$_3$C(CN)), 19.83 (*C*H$_2$CH$_2$CO) ppm; IR (CH_3Cl): $\bar{\nu}$ = 2240, 1730, 1580, 1380 cm^{-1}.

6,6′-azobis-(6-cyanoheptanoic) acid chloride
(**3c;** $C_{16}H_{22}N_4Cl_2O_2$)
Yield: 57%; m.p.: 91–93 °C; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 2.98–2.89 (*t, J* = 7.2 Hz, 4H, C*H*$_2$CO), 2.23–2.11 (m, 2H, C*H*$_2$), 2.10–1.97 (m, 2H, C*H*$_2$), 1.83–1.64 (m, 4H, C*H*$_2$), 1.71 (s, 6H, C*H*$_3$), 1.63–1.46 (m, 2H, C*H*$_2$), 1.44–1.22 (m, 2H, C*H*$_2$) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 180.37 (*C*OCl), 119.48 (*C*N), 69.74 (*C*(CN)), 46.59 (*C*H$_2$CO), 37.37 (*C*H$_2$C(CN)), 24.72 (*C*H$_2$CH$_2$CO), 23.86 (*C*H$_3$C(CN)), 23.22 (*C*H$_2$CH$_2$C(CN)) ppm; IR (CH_2Cl_2): $\bar{\nu}$ = 2260, 1720, 1490, 1380 cm^{-1}.

Preparation of azo-peroxyesters; general procedure

The solution of hydroperoxide (0.05 mol) in CH_2Cl_2 was cooled down to less than 5 °C, and aqueous solution of sodium hydroxide (0.05 mol) was slowly added after extensive stirring so that the temperature of the mixture was below 5 °C. A suspension of sodium salt of hydroperoxide was formed. To this mixture a solution of azo acid chloride (0.01 mol) (**3a–c**) in $\mathrm{CH_2Cl_2}$ was added. The progress of the reaction was studied by means of the TLC method (mobile phase $\mathrm{CH_2Cl_2{:}CH_3COCH_3}$ 9:1; a solution of sodium iodide in acetic acid was used for visualization of the separated substances). The reaction was continued for 1.5 h. The mixture was then washed twice: with water, 20% aqueous solution of NaOH, 5% aqueous solution of $\mathrm{NaHCO_3}$, and finally twice with water. The organic layer was dried with $\mathrm{MgSO_4}$, and then the solvent was evaporated on vacuum rotary of ambient temperature. All azo-peresters was crystallized from $\mathrm{CH_2Cl_2}$.

Di-tert-butyl-4,4′-azobis-(4-cyanoperoxypentanoate)
(**4a**; $\mathrm{C_{20}H_{32}N_4O_6}$)
Yield: 77%; m.p.: 101–104 °C Ref. [13]: m.p.: 104–106 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, δ, 300 MHz): 2.54–2.47 (m, 4H, $\mathrm{C}\mathit{H}_2$), 2.44–2.33 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.71 (s, 6H, $\mathrm{C}\mathit{H}_3\mathrm{C(CN)}$), 1.31 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, δ, 75 MHz): 168.89 ($\mathit{C}\mathrm{OO}$), 117.16 ($\mathit{C}\mathrm{N}$), 83.87 ($\mathit{C}\mathrm{(CH_3)_3}$), 71.76 ($\mathit{C}\mathrm{(CN)}$), 32.90 ($\mathit{C}\mathrm{H_2C(CN)}$), 26.19 ($(\mathit{C}\mathrm{H_3})_3\mathrm{C}$), 26.12 ($\mathit{C}\mathrm{H_3C(CN)}$), 23.83 ($\mathit{C}\mathrm{H_2CO}$); IR ($\mathrm{CH_2Cl_2}$): $\bar{\nu}$ = 2990, 2250, 1780, 1480, 1380 cm^{-1}.

Di-tert-amyl-4,4′-azobis-(4-cyanoperoxypentanoate)
(**5a**; $\mathrm{C_{22}H_{36}N_4O_6}$)
Yield: 42%; m.p.: 87–89 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, δ, 300 MHz): 2.58–2.32 (m, 8H, $\mathrm{C}\mathit{H}_2$), 1.74 (s, 6H, $\mathrm{C}\mathit{H}_3\mathrm{CCN}$), 1.69–1.59 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.27 (s, 12H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{C}$), 0.95–0.90 (*t*, *J* = 7.5 Hz, 6H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, δ, 75 MHz): 168.87 ($\mathit{C}\mathrm{OO}$), 117.15 ($\mathit{C}\mathrm{N}$), 86.20 ($\mathit{C}\mathrm{(CH_3)_2C_2H_5}$), 71.74 ($\mathit{C}\mathrm{(CN)}$), 32.92 ($\mathit{C}\mathrm{H_2CH_3}$), 31.37 ($(\mathit{C}\mathrm{H_2})\mathrm{CCN}$), 26.17 ($\mathit{C}\mathrm{H_2CO}$), 23.73 ($(\mathit{C}\mathrm{H_3})\mathrm{CCN}$), 23.42 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2C_2H_5}$), 8.16 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$) ppm; IR ($\mathrm{CH_2Cl_2}$): $\bar{\nu}$ = 2985, 2240, 1760, 1460, 1370 cm^{-1}.

Di-tert-butyl-5,5′-azobis-(5-cyanoperoxyhexanoate)
(**4b**; $\mathrm{C_{22}H_{36}N_4O_6}$)
Yield: 78%; m.p.: 102–104 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, δ, 300 MHz): 2.43–2.38 (m, 4H, $\mathrm{C}\mathit{H}_2$), 2.25–2.04 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.95–1.77 (m, 2H, $\mathrm{C}\mathit{H}_2$); 1.72 (s, 6H, $\mathrm{C}\mathit{H}_3$), 1.69–1.60 (m, 2H, $\mathrm{C}\mathit{H}_2$), 1.32 (s, 18H, $(\mathrm{C}\mathit{H}_3)_3\mathrm{C}$) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, δ, 75 MHz): 169.86 ($\mathit{C}\mathrm{OO}$), 117.76 ($\mathit{C}\mathrm{N}$), 83.53 ($\mathit{C}\mathrm{(CH_3)_3}$), 72.23 ($\mathit{C}\mathrm{(CN)}$), 37.17 ($\mathit{C}\mathrm{H_2C(CN)}$), 30.37 ($\mathit{C}\mathrm{H_2CO}$), 26.07 ($(\mathit{C}\mathrm{H_3})_3\mathrm{C}$), 23.98 ($\mathit{C}\mathrm{H_3(C)CN}$), 19.57 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$) ppm; IR ($\mathrm{CH_2Cl_2}$): $\bar{\nu}$ = 2980, 2250, 1775, 1460, 1360 cm$^{-1.}$

Di-tert-amyl-5,5′-azobis-(5-cyanoperoxyhexanoate)
(**5b**; $\mathrm{C_{24}H_{40}N_4O_6}$)
Yield: 69%; m.p.: 76–78 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, δ, 300 MHz): 2.36–2.32 (*t*, *J* = 7.05 Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.18–1.97 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.86–1.72 (m, 2H, $\mathrm{C}\mathit{H}_2$), 1.65 (s, 6H, $\mathrm{C}\mathit{H}_3$), 1.62–1.49 (m, 6H, $\mathrm{C}\mathit{H}_2$), 1.19 (s, 12H, $\mathrm{C(C}\mathit{H}_3)_2\mathrm{C_2H_5}$), 0.88–0.83 (*t*, *J* = 7.5 Hz, 6H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, δ, 75 MHz): 169.70 ($\mathit{C}\mathrm{OO}$), 117.54 ($\mathit{C}\mathrm{N}$), 85.61 ($\mathit{C}\mathrm{(CH_3)_2C_2H_5}$), 72.00 ($\mathit{C}\mathrm{(CN)}$), 36.89 ($\mathit{C}\mathrm{H_2CH_3}$), 31.13 ($\mathit{C}\mathrm{H_2C(CN)}$), 25.80 ($\mathit{C}\mathrm{H_2CO}$), 23.44 ($\mathit{C}\mathrm{H_3C(CN)}$), 23.15 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2C_2H_5}$), 19.34 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 7.95 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$) ppm; IR ($\mathrm{CH_2Cl_2}$): $\bar{\nu}$ = 2985, 2240, 1765, 1455, 1380 cm$^{-1.}$

Di-tert-butyl-6,6′-azobis-(6-cyanoperoxyheptanoate)
(**4c**; $\mathrm{C_{24}H_{40}N_4O_6}$)
Yield: 79%; m.p.: 107–109 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, δ, 300 MHz): 2.37–2.32 (m, 4H, $\mathrm{C}\mathit{H}_2$), 2.20–1.97 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.79–1.66 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.69 (s, 6H, $\mathrm{C}\mathit{H}_3$), 1.61–1.36 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.32 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, δ, 75 MHz): 170.36 ($\mathit{C}\mathrm{OO}$), 118.00 ($\mathit{C}\mathrm{N}$), 83.38 ($\mathit{C}\mathrm{(CH_3)_3}$), 72.45 ($\mathit{C}\mathrm{(CN)}$), 37.68 ($\mathit{C}\mathrm{H_2C(CN)}$), 30.74 ($\mathit{C}\mathrm{H_2CO}$), 26.09 ($(\mathit{C}\mathrm{H_3})_3\mathrm{C}$), 24.40 ($\mathit{C}\mathrm{H_2}$), 24.04 ($\mathit{C}\mathrm{H_3(C)CN}$), 23.71 ($\mathit{C}\mathrm{H_2}$) ppm; IR ($\mathrm{CH_2Cl_2}$): $\bar{\nu}$ = 2980, 2250, 1775, 1460, 1360 cm$^{-1.}$

Di-tert-amyl-6,6′-azobis-(6-cyanoperoxyheptanoate)
(**5c**; $\mathrm{C_{26}H_{44}N_4O_6}$)
Yield: 76%; m.p.: 87-89 °C; ^{1}H NMR ($\mathrm{CDCl_3}$, δ, 300 MHz): 2.29–2.24 (*t*, *J* = 7.35 Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.14–1.92 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.72–1.39 (m, 4H, $\mathrm{C}\mathit{H}_2$), 1.63 (s, 12H, $\mathrm{C(C}\mathit{H}_3)_2\mathrm{C_2H_5}$), 1.38–1.15 (m, 8H, $\mathrm{C}\mathit{H}_2$), 1.19 (s, 6H, $\mathrm{C}\mathit{H}_3$), 0.88–0.83 (*t*, *J* = 7.65 Hz, 6H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, δ, 75 MHz): 170.33 ($\mathit{C}\mathrm{OO}$), 118.01 ($\mathit{C}\mathrm{N}$), 85.72 ($\mathit{C}\mathrm{(CH_3)_2C_2H_5}$), 72.46 ($\mathit{C}\mathrm{(CN)}$), 37.69 ($\mathit{C}\mathrm{H_2CH_3}$), 31.40 ($\mathit{C}\mathrm{H_2C(CN)}$), 30.78 ($\mathit{C}\mathrm{H_2CO}$), 26.09 ($\mathrm{CH_2CH_2CH_2CH_2CO}$), 24.40 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2C_2H_5}$), 24.04 ($\mathit{C}\mathrm{H_3C(CN)}$), 23.70 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_2CO}$), 8.21 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$) ppm; IR ($\mathrm{CH_2Cl_2}$): $\bar{\nu}$ = 3020, 2280, 1775, 1450, 1380 cm^{-1}.

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References

1. Engel PS, Ying Y, He SL (2003) Macromolecules 36:3821
2. Hazer B, Ayas A, Besirli N, Saltek N (1989) Makromol Chem 190:1987
3. Engel PS, He SL, Smith WB (1997) J Am Chem Soc 119:6059
4. Simionescu CrI, Popa AA (1992) Polym-Plast Technol Eng 31:451
5. Vogla C, Hazer B, Torul O (1997) Eur Polym J 33:907
6. Simionescu CrI, Comanita E, Pastravanu M, Dumitriu S (1986) Prog Polym Sci 12:1
7. Liao WP, Chen F (1992) US Pat 5.108.622
8. Engel PS, He SL, Ch Wang, Duan S, Smith WB (1999) J Am Chem Soc 121:6367
9. Ivantschew SS (1979) Plaust Kautschuk 26:121
10. Schulz M, West G (1974) J Prakt Chemie 316:581
11. Simionescu CrI, Sik KG, Comanita E, Dumitriu S (1984) Eur Polym J 20:467
12. Piirma I, Chou LP (1979) J Appl Polym Sci 24:2051
13. Sheppard ChS (1978) US Pat 4.088.642

14. Simionescu CrI, Comanita E, Dumitriu S, Petrovici A, Shaikh AS (1982) Revista de Chimie 33:423
15. Shaikh AS, Comanita E, Dumitriu S, Simionescu CrI (1981) Die Angew Makromol Chem 100:147
16. Kharasch MS, Fono A (1959) J Org Chem 24:72
17. Bates HA, Deng PN (1983) J Org Chem 48:4479
18. Schaeffer JR, Snoddy AO (1963) Org Syntheses Coll 4:19