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2-Cyano-2-butylazoformamidoethyl 4-*t*-butylazo-4-cyanopentanoate synthesis and its behaviour in methyl methacrylate polymerization

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SYNOPSIS

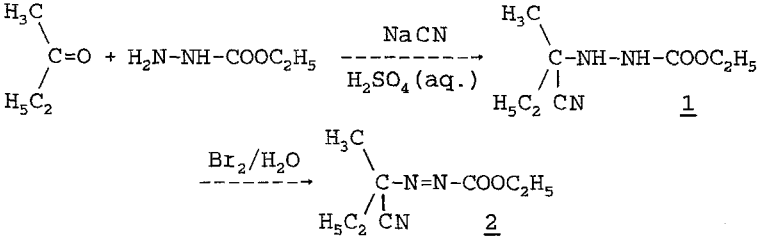
In the present paper the synthesis of a new bis-azo initiator, 2-cyano-2-butylazo-formamidoethyl 4-t-butylazo-4-cyanopentanoate, is reported. The structures of the intermediates and of the initiator were confirmed by the IR and ^{1}H-NMR spectral measurements. The polymerization of methyl methacrylate (MMA) in the presence of this initiator was studied and the conversion-time dependence followed with different concentrations of the initiator and of the monomer.

INTRODUCTION

The aliphatic ketones, as well as keto acids, react with hydrazine or its monosubstituted derivatives in the presence of sodium cyanide leading to cyanoalkyl hydrazines, which are readily oxidized to azo compounds [1-3]. A typical approach is the synthesis of 4-carbetoxihydrazo-4-cyanopentanol from ethyl carbazate, 4-ketopentanol and NaCN, which has been achieved in order to obtain a bifunctional polymerization initiator [4]. The nucleophilic properties of ethyl carbazate amino group affords reactions with aliphatic ketones, as methyl ethyl ketone, leading to useful intermediates for synthesis of bis-azo compounds.

RESULTS AND DISCUSSION

Methyl ethyl ketone reacts with ethyl carbazate and NaCN in acidic medium, via condensation to hydrazone, followed by HCN addition. Ethyl 2-cyano-2-butylhydrazocarboxilate (1) is subsequently oxidized with bromine to the corresponding azo derivative (2).



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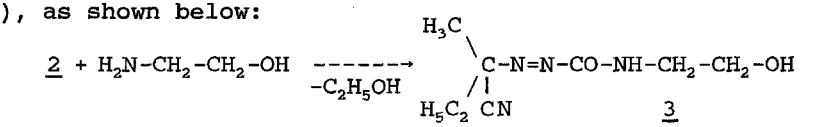
The oxidation requires the use of an organic solvent in order to dissolve the hydr azoderivative.

As well as ethyl azodicarboxylate [5], the azo ester (2) undergoes reaction with ethanolamine, under cold conditions, resulting in N-(β-hydroxyethyl)-2-cyano-2-butylazoformamide (3), as shown below:



The structure of the intermediates 1-3 is confirmed by the elemental analysis data, IR and ^{1}H-NMR spectroscopy.

Figure 1 presents the ^{1}H-NMR spectra of the compound (3).

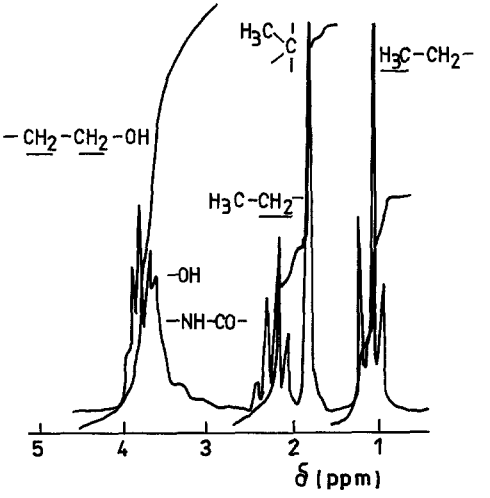
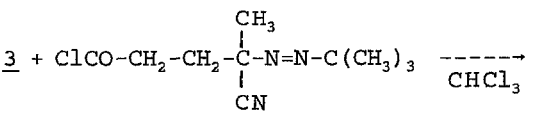


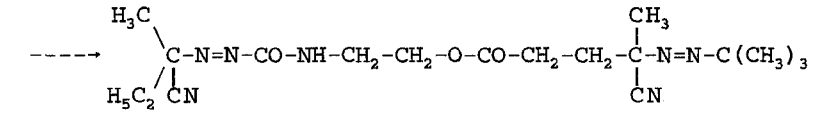
Fig. 1 - ^{1}H-NMR spectra of N-(β-hydroxyethyl)-2-cyano-2-butylazoformamide.

The alcoholic group from ethanolamine residue is conveniently exploated in the reaction with an acylating azo derivative in order to obtain a bis-azo compound, which might act as a bifunctional sequential initiator.

The 4-t-butylazo-4-cyano pentanoic acid chloride has been used as acylating azo component; it is a relatively low temperature thermolabile intermediate.

The reaction is the following:





The condensation is carried out in anhydrous organic solvent, using pyridine as hydrochloric acid acceptor. The initiator containing solution is successively washed with cold dilute H_2SO_4 and Na_2CO_3 solutions and dried on Na_2SO_4, the solvent being finally removed under low pressure. At last the substance is further purified on an alumina chromatographic column by using ethyl acetate as eluent.

The envisaged formula is supported by elemental, IR and ^{1}H-NMR analyze.

Figure 2 reproduces the ^{1}H-NMR spectra in $CDCl_3$.

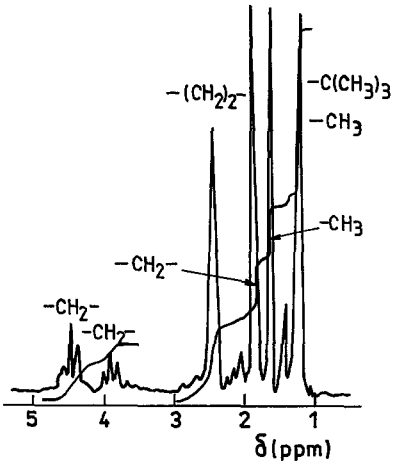


Fig. 2 - ^{1}H-NMR spectra of 2-cyano-2-butylazoformamidoethyl 4-t-butylazo-4-cyanopentanoate.

The structure of the initiator suggests the possibility of sequential thermolysis, due to the stabilization of one of the azo groups through electron delocalization on the neighbouring carbonyl group.

Consequently, a kinetic study of the MMA polymerization in the presence of a synthetized initiator has been carried out and the conversion followed in time at different initiator and monomer concentrations.

The runs were made at 75°C which limitates the decomposition of the initiator at the dialkylazo group.

The conversion-time dependence at different initiator and monomer concentrations is depicted in Figs. 3-4.

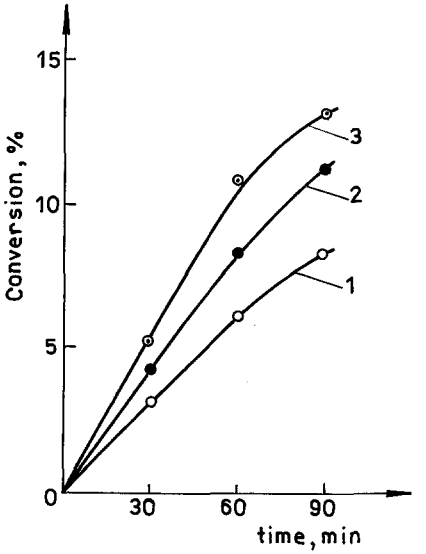


Fig. 3 - The influence of polymerization time on conversion at different concentrations of the initiator, in benzene. t = 75°; [M] = 3 mole/l; curves 1, 2, 3: [I] = $1.536 \cdot 10^{-3}$ mole/l; [I] = $3.051 \cdot 10^{-3}$ mole/l; [I] = $4.748 \cdot 10^{-3}$ mole/l.

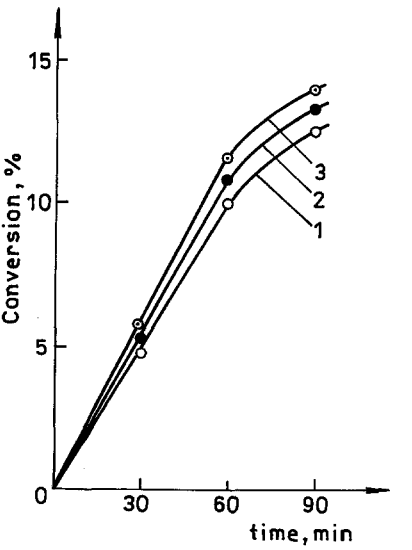


Fig. 4 - The influence of polymerization time on conversion at different concentrations of the monomer, in benzene. t = 75°; [I] = $4.748 \cdot 10^{-3}$ mole/l; curves 1, 2, 3: [M] = 2.5 mole/l; 3 mole/l; 3.5 mole/l.

The partial reaction orders with respect to the initiator and the monomer are of 0.48 and 1.25, respectively, which is in a fairly good agreement with the theoretical predictions on the radical polymerization.

Finally, some polymerizations within the 75-85°C temperature range have been carried out at constant initiator and monomer concentrations (Fig. 5).

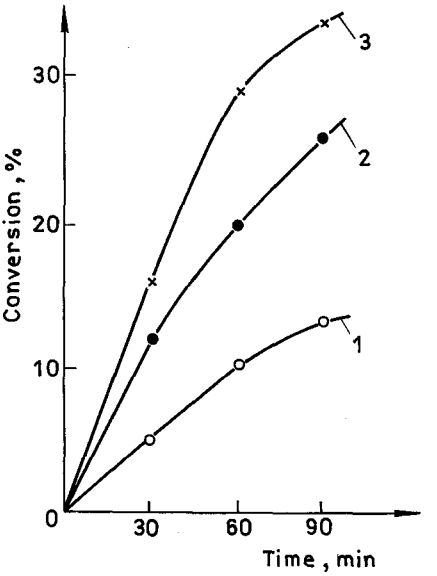


Fig. 5 - The influence of reaction time on conversion, at different temperatures: (1) 75°; (2) 80°; (3) 85°. [I] = $4.748 \cdot 10^{-3}$ mole/l; [M] = 3 mole/l.

A stepwise increase in the conversion at 80°C and 85°C can be noticed, which suggests a partial decomposition of the initiator second azo group.

The synthetized "active" polymers lead themselves to block copolymer synthesis, which will be treated in a subsequent paper.

EXPERIMENTAL

BACP chloride is prepared from BACP acid and PCl_5 in anhydrous benzene, at low temperature.

Ethyl 2-cyano-2-butylhidrazocarboxylate (1)

4.9 g (0.1 mole) of NaCN dissolved in 20 ml water and 7.2 g (0.1 mole) methyl ethyl ketone are added to a solution of 10.4 g (0.1 mole) ethyl carbazate in 25 ml water. A solutions of 5 ml conc. H_2SO_4 in 20 ml water is then added dropwise within an hour time and the reaction mixture kept at the room tempera-

ture for 3-4 hours when a white crystalline product separates. The flask is allowed to stay over night at room temperature, and the crystalline solid is filtered. M.p. 75°C (from water, CH_2Cl_2 and n-heptane) IR: 1730 cm^{-1} (ν_{CO}), 2235 cm^{-1} (ν_{CN}), 3120 and 3240-3310 cm^{-1} (ν_{NH}), 2875 and 2995 cm^{-1} (ν_{CH}).

Analyses:	$C_8H_{15}N_3O_2$ (185)		
Calc:	C 51.89;	H 8.10;	N 22.70
Found:	C 51.61;	H 8.24;	N 22.39

Ethyl 2-cyano-2-butylazocarboxylate (2)

3.7 g (0.2 mole) hydrazo derivative (1) in 45 ml chloroform and 18 ml water are treated with bromine (approximately 1.1 ml). By treating the reaction mixture with some $NaHSO_3$ solution in a funnel, the organic layer separates which is then washed with cold water and dried on anhydrous Na_2SO_4. The solvent is finally removed under low pressure. Yield 3.5 g (95%) IR: 1773 cm^{-1} (ν_{CO}), 2895, 2950 and 2995 cm^{-1} (ν_{CH}). NMR, ppm: 1.1 ($\underline{CH_3}-CH_2-\overset{|}{\underset{|}{C}}-CN$, triplet); 1.47 ($\underline{CH_3}-CH_2-O-$, triplet); 1.75 ($CH_3-\overset{|}{\underset{|}{C}}-CN$, singlet); 2.12 ($-CH_2-\overset{|}{\underset{|}{C}}-CN$, quartet); 4.3-4.75 ($-CH_2-O-$, quartet).

Analyses:	$C_8H_{13}N_3O_2$ (183)		
Calc:	C 52.45;	H 7.10;	N 22.95
Found:	C 52.15;	H 7.25;	N 22.71

N-(β-Hydroxyethyl)-2-cyano-2-butylazoformamide (3)

9.15 g (0.05 mole) azo derivative (2) in 75 ml ethanol are treated under cooling with 3.05 ml (0.05 mole) ethanolamine in 10 ml ethanol. The solution is stirred for 2-3 hours and left over night. After removal of the solvent under low pressure an yellow oil is obtained which crystallizes in time in the refrigerator. The oily product is solved in chloroform, treated with hexane and allowed to recrystallize in the refrigerator. Yield 9 g (91%). M.p. 40°C. IR: 1730 cm^{-1} (ν_{CO}), 2245 cm^{-1} (ν_{CN}), 3340 cm^{-1} (ν_{NH}), 3480 cm^{-1} (ν_{OH}), NMR, ppm: 1.05 ($\underline{CH_3}-CH_2-\overset{|}{\underset{|}{C}}-CN$, triplet); 1.8 ($CH_3-\overset{|}{\underset{|}{C}}-CN$, singlet); 2.15 ($-CH_2-\overset{|}{\underset{|}{C}}-CN$, quartet); 3.45-4.00 ($-CH_2-CH_2-$, multiplet).

Analyses:	$C_8H_{14}N_4O_2$ (198)		
Calc:	C 48.48;	H 7.07;	N 28.28
Found:	C 48.29;	H 7.25;	N 28.03

2-Cyano-2-butylazoformamidoethyl 4-(t-Butylazo-4-Cyano-pentanoate (4)

9.9 g (0.05 mole) azo alcohol (3) and 20 ml anhydrous chloroform cooled to 0-5°C are treated with 3.95 g (0.05 mole) pyridine. Subsequently, the BACP chloride resulted from 10.55 g (0.05 mole) BACP acid, solved in 30 ml chloroform, is added dropwise within 1.5 hours. The reaction mixture is stirred for another 3-4 hours and allowed to stay over night. The chloroformic solution is successively washed with water, dilute H_2SO_4 and Na_2CO_3 solutions and again with water. After drying on anhydrous Na_2SO_4 and removal of solvent under low pressure, an yellow oil results, which crystallizes by cooling. The product is purified on an Al_2O_3 chromatographic column, using ethyl acetate as eluent. M.p. 49-51°C IR: 1725 cm^{-1} (ν_{CO} amide), 1750 cm^{-1} (ν_{CO} ester), 2250 cm^{-1} (ν_{CN}), 2875, 2945 and 2980 cm^{-1} (ν_{CH}), 3920 cm^{-1} (ν_{NH}), NMR, ppm: 1.3 ($\underline{CH_3}-CH_2-\overset{|}{\underset{|}{C}}-CN$, triplet), 1.3 ($(CH_3)_3C-$, singlet); 1.67 ($-CH_2-\overset{|}{\underset{|}{C}}-N=$, singlet); 1.88 ($CH_3-\overset{|}{\underset{|}{C}}-CN$, singlet); 2.10 ($-CH_2-\overset{|}{\underset{|}{C}}-CN$, quartet); 2.5 ($-\overset{|}{\underset{|}{C}}-CH_2-CH_2-\overset{|}{\underset{|}{C}}-N=$, multiplet); 3.88 ($-CH_2-NH-$, triplet; 4.45 ($-CH_2-O-$, triplet).

Analyses: $C_{18}H_{29}N_7O_3$ (391)

Calc: C 55.24; H 7.61; N 25.06

Found: C 55.01; H 7.64; N 25.12

MMA Polymerization with initiator (5)

The required amounts of monomer, initiator and solvent (benzene) added till 10 ml are sealed under inert atmosphere in glass ampules and heated on a water bath at the prescribed temperatures and reaction times. The polymer is precipitated in methanol acidified by HCl, filtered and dried at 40°C under vacuum. The conversion is estimated gravimetrically.

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