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Abstract

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SYNTHESIS OF POLYMERS FROM NITRILES OF AROMATIC AND ALIPHATIC ACIDS BY THE POLYRECOMBINATION REACTION

In continuation of previously carried out studies of the polyrecombination reaction of nitriles of fatty and aromatic acids (1,2), benzonitrile, i.e., a compound in which mobile hydrogen atoms are absent, was treated with tert-butyl peroxide. Nevertheless, as a result of the reaction carried out, along with a large amount of unreacted starting material, polymeric products were obtained. When the amount of peroxide taken was increased from 1 mole to 2.7 moles per mole of benzonitrile, the yields (from 13.9% to 65%), softening temperature (from 140 to 280° C), and molecular weights (from 1075 to 20850) of the polymers increased.

Proceeding from the great tendency toward methylation of benzene derivatives with strong electron-acceptor substituents (3), it could be assumed that methylation of benzonitrile occurs initially, and that the polymer is formed from the corresponding tolunitriles. The small amount of tert-butyl alcohol formed as a result of the reaction indicates decomposition of the greater part of the butoxyl radicals according to the reaction $(CH_3)_3CO^{\cdot} \rightarrow \dot{CH}_3 + CH_3COCH_3$. The data of elemental analysis and IR spectra of the polymers obtained agree well with the previously found data of elemental analysis and IR spectra of the polymer from 4-tolunitrile (2). Examination of the benzonitrile that had not entered into the reaction by IR spectra and NMR (proton shift relative to benzene equal to $50 \cdot 10^{-7}$ abs. units) showed the presence of a CH_3 group bonded to the benzene ring. Chromatographic analysis of the benzonitrile from the reaction also established the presence in it of 2- and 4-tolunitriles, with 2-tolunitrile present in greater amount than 4-tolunitrile. It was found that with an increase in the amount of peroxide taken, not only does the molar ratio of the sum of 2- and 4-tolunitriles to benzonitrile change, but the amount of 2-tolunitrile also increases relative to 4-tolunitrile in the reaction mixture.

Joint polyrecombination of 2- and 4-tolunitriles showed that the ratio of the 2- and 4-isomers does not change in the course of the reaction. It follows from this that the increase in the amount of 2-tolunitrile relative to 4-tolunitrile, formed during the polyrecombination of benzonitrile, is caused by the greater tendency of benzonitrile toward methylation in the ortho position. The results found agree with the data obtained by Heem and co-workers (4), who established a greater tendency toward homolytic substitution of hydrogen in the ortho position compared with hydrogen in the para position.

Thus, the formation of polymer from benzonitrile may be represented by the scheme:

$$C_6H_5CN \xrightarrow{CH_3^{\cdot}} CH_3C_6H_4CN + CH_3C_6H_4CN \xrightarrow{R^{\cdot}} \cdots{-}CH(C_6H_4CN){-}CH(C_6H_4CN){-}\cdots$$

To solve another problem posed in the present work (the synthesis of copolymers from nitriles of aliphatic acids), two nitriles were treated with tert-butyl peroxide. The properties of the polymers of the selected nitriles had been studied previously (1,2). In one case, diphenylmethane was taken instead of a nitrile. The results of the synthesis of copolymers are presented in Table 1. Thermomechanical

Table 1

Starting compounds	Molar ratio, I/II	Molar ratio of peroxide : starting compd.	Proposed structure of the copolymer obtained	Copolymer yield, %	Molecular weight of copolymer	Decomp. temp. of copolymer, °C	E.p.r. data: ΔH, oerst.	E.p.r. data: N, spins/g
Starting compounds	Molar ratio, I/II	Molar ratio of peroxide : starting compd.	Proposed structure of the copolymer obtained	Copolymer yield, %	Molecular weight of copolymer	Decomp. temp. of copolymer, °C	E.p.r. data: ΔH, oerst.	E.p.r. data: N, spins/g
I. Malononitrile II. Adiponitrile	1	0.95	[structural formula not reproducible in text] [[unclear: displayed structural formula of copolymer, with substituent note]]where $R = -(CH_2)_3CN$ Found, %: C 61.27; 60.97; H 5.30; 5.25; N 26.46; 26.60 Calculated	48.9	11500	600	6	$1 \cdot 10^{18}$

Starting compounds	Molar ratio, I/II	Molar ratio of peroxide : starting compd.	Proposed structure of the copolymer obtained	Copolymer yield, %	Molecular weight of copolymer	Decomp. temp. of copolymer, °C	E.p.r. data: ΔH, oerst.	E.p.r. data: N, spins/g
I. Malononitrile II. Benzyl cyanide	1	0.98	[structural formula not reproducible in text] [[unclear: displayed structural formula of copolymer, with substituent note]] where $R_1 = -C_6H_4OC(CH_3)_3$ Found, %: C 64.80; 64.95; H 4.4; 4.71; N 21.89; 21.60 Calculated, %: C 64.79; H 5.83; N 21.17	46.3	4570*	600	6	$1 \cdot 10^{18}$

Starting compounds	Molar ratio, I/II	Molar ratio of peroxide : starting compd.	Proposed structure of the copolymer obtained	Copolymer yield, %	Molecular weight of copolymer	Decomp. temp. of copolymer, °C	E.p.r. data: ΔH, oerst.	E.p.r. data: N, spins/g
I. Malononitrile II. Diphenylmethane	2	0.97	[structural formula not reproducible in text] [[unclear: displayed structural formula of copolymer]] Found, %: C 72.23; 72.03; H 5.18; 5.12; N 21.89; 21.60 Calculated, %: C 72.00; H 5.00; N 21.00	84.9	5200	550	6	$2 \cdot 10^{18}$

Starting compounds	Molar ratio, I/II	Molar ratio of peroxide : starting compd.	Proposed structure of the copolymer obtained	Copolymer yield, %	Molecular weight of copolymer	Decomp. temp. of copolymer, °C	E.p.r. data: ΔH, oerst.	E.p.r. data: N, spins/g
I. Methyl cyanoacetateII. Benzyl cyanide	1	1.79	[structural formula not reproducible in text] [[unclear: displayed structural formula of copolymer, with substituent note]]where $R_2 = -C(=O)OCH_3$; $R_3 = -C_6H_4CH_3$Found, %: C 68.98; 69.15; H 5.81; 5.84; N 13.82; 13.68Calculated, %: C 68.76; H 4.27; N 12.58	11.1	12200	300	7	$4 \cdot 10^{17}$

Starting compounds	Molar ratio, I/II	Molar ratio of peroxide : starting compd.	Proposed structure of the copolymer obtained	Copolymer yield, %	Molecular weight of copolymer	Decomp. temp. of copolymer, °C	E.p.r. data: ΔH, oerst.	E.p.r. data: N, spins/g
I. Methyl cyanoacetateII. Malononitrile	1	0.93	[structural formula not reproducible in text] [[unclear: displayed structural formula of copolymer, with substituent note]]where $R_2 = -C(=O)OCH_3$Found, %: C 51.92; 51.95; H 5.49; 5.66; N 21.81; 22.00Calculated, %: C 52.62; H 3.78; N 22.17	72.8	7880	600	5	$1 \cdot 10^{18}$

Fig. 1. Thermomechanical curves of copolymers based on: a —malononitrile and adiponitrile; —malononitrile and cyanobenzene; —malononitrile and diphenylmethane; —methyl cyanoacetate and benzyl cyanide; —methyl cyanoacetate and malononitrile

Figure 1: Fig. 1. Thermomechanical curves of copolymers based on: a —malononitrile and adiponitrile; —malononitrile and cyanobenzene; —malononitrile and diphenylmethane; —methyl cyanoacetate and benzyl cyanide; —methyl cyanoacetate and malononitrile

* The molecular weight of the copolymer insoluble in acetone is 9200 (76.4% of the total amount of copolymer). All molecular weights were determined isopiestically in dimethylformamide.

the curves for the resulting copolymers are given in Fig. 1. All copolymers are soluble in dimethylformamide and cresol.

In connection with the synthesis of copolymers from nitriles of aliphatic acids, it seemed advisable to us to carry out additional studies to clarify the structure of the previously obtained polymer from malonic acid dinitrile (1), for which it had been shown that the polyrecombination reaction is not the principal process of chain growth. We found that malononitrile is converted into a polymer even in the absence of peroxide, upon prolonged heating at 200°. The polymer is a black powder, partially soluble in dimethylformamide, unchanged on heating to 700°, and contains about 40% nitrogen. In the IR spectrum there is absorption at 2250 cm^{-1}, characteristic of free nitrile groups. Other nitrile groups probably take part in the formation of the polymer. In the presence of small amounts of peroxide, the polymerization of malononitrile is accelerated.

Fig. 1. Thermomechanical curves of copolymers based on: *a* —malononitrile and adiponitrile; —malononitrile and cyanobenzene; —malononitrile and diphenylmethane; —methyl cyanoacetate and benzyl cyanide; —methyl cyanoacetate and malononitrile.

The presence of a system of conjugated $C = N$ bonds in the polymer is indicated by the result of treating the polymer with an aqueous solution of silver nitrate according to the method of Volker and Zinna (5). The precipitate appearing as a result of such treatment of the polymer from malononitrile is analogous to the precipitate found by these authors for heat-treated polymethacrylonitrile and polyacrylonitrile.

The NMR spectra data for the polymer and the starting malonic acid dinitrile confirmed the fact, previously established with the aid of IR spectra, that the CH_2 group is retained in the polymer. For the polymer, the chemical shift of the protons relative to benzene is $36.6 \cdot 10^{-7}$ abs. units, which corresponds to the chemical shift of the protons of malononitrile ($34 \cdot 10^{-7}$ abs. units).

Experimental Part

The constants of all substances used in the work correspond to the literature data. The polyrecombination reaction was carried out by the previously described procedure (6). In experiments with benzonitrile, the polymer was precipitated from benzene (50 ml) with petroleum ether (250 ml). Benzonitrile was distilled off from the filtrate at 95—130°/3—5 mm Hg. Copolymers from nitriles of aliphatic acids were precipitated from dimethylformamide (50 ml) into methanol (200 ml).

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Note: Figure translations are in progress. See original paper for figures.