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Abstract

Full Text

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SYNTHESIS OF POLYESTERS CONTAINING TRIPLE BONDS IN THE CHAIN

In the present work, investigations are continued ([1,2]) on the synthesis and study of the properties of polyesters obtained by joint oxidative condensation of mono- and dipropargyl esters with *p*-diethynylbenzene.

As starting products we used dipropargyl esters of 4,4′-dioxydiphenyl, 4,4′-dioxydiphenyl-2-propane, hexafluoro-2,2-bis-(4-oxyphenyl)-propane, and propargyl esters of benzoic acid, phenol, and quinizarin. The choice of the above-mentioned esters is due to the fact that preliminary investigations of the polymers obtained on the basis of dipropargyl esters showed the absence of certain electrophysical properties (for example, photo-e.m.f.) characteristic of conjugated polyynes. We hoped, by introducing a molecule of *p*-diethynylbenzene into the polyester chain, to alter the electrophysical properties of the polyesters.

It had previously been shown ([3]) that introduction of terminal groups (using phenylacetylene and *p*-diethynylbenzene as examples) into the polyyne chain leads to the formation of a polymer of crystalline structure.

As a result of joint oxidative dehydropolycondensation of dipropargyl esters with *p*-diethynylbenzene, mainly insoluble products were obtained. The experimental data are summarized in Table 2.

Table 1

Data from the IR spectra of the copolymers

Polymer based on	$-\langle\!=\!\rangle-$	$\equiv$ CH	$-C\equiv$ C–	$-\overset{\|}{\underset{\|}{C}}-$ O– C–	$\overset{\|}{\underset{\|}{C}}=$ O	$[CH_3]_2C<$	$<CH_2-$	$-\overset{CF_3}{\underset{CF_3}{\overset{\|}{\underset{\|}{C}}}}-$
p-Diethynylbenzene	830 960 1200 1800 3300	3300	2200	–	–	–	–	–

Polymer based on	$-\langle\!=\!\rangle-$	$\equiv$ CH	$-C\equiv$ C–	$-$C$-$ O $-$ C–	C $=$ O	$[CH_3]_2C-\!\!<$	$-CH_2-$	CF_3 | $-C-$ | CF_3	
p-Diethynylbenzene and propargyl benzoate	8359	6310	2010	95	3300	2235	2315	1110	1725	–	1460	–
p-Diethynylbenzene and propargyl ether of quinizarin	8359	5010	2010		3270	2105	2140	**2210**	–	–	1440	–
p-Diethynylbenzene and dipropargyl ether of dioxydiphenyl	8359	7710	2010		3280	2125		1110	–	–	1460	–
p-Diethynylbenzene and dipropargyl ether of dioxydiphenylpropane	8351	0201	0901		3290	2200	2235	**2340**	–	1188	1450	–

Polymer based on	$-\Leftarrow\rangle-$	$\equiv$CH	$-C\equiv$C–	$-C-$O$-$C–	C=O	$[CH_3]_2C-\prec CH_2-$	–	CF_3 | –C– | CF_3	
p-Diethynylbenzene and dipropargyl ether of hexafluoropropane	830	980	1020	3300	1130	–	–	1440	1310 1170 1130

For the synthesized polymers, IR spectra* were recorded. In all samples there remain absorption bands characteristic of the IR spectrum of the product of oxidative polydehydrocondensation of *p*-diethynylbenzene ([4]).

* The IR spectra were recorded in the optical laboratory of INEOS, Academy of Sciences of the USSR, by N. A. Chumaevskii, to whom the authors express their deep gratitude.

Table 2

Starting substances	Quantity, g	Quantity, mol	Reaction duration, h	Polymer yield, g	Polymer color	Polymer structure	Calculated, % C	Calculated, % H	Found, % C	Found, % H	Other found value, %
1. HC≡C−CH_2−O−[[structural formula: fused aromatic system]]−O−CH_2−C≡CHDEB*	0.4	0.6	0.043	0.048	3	7.5	yellow	−C≡C−[[structural formula: aromatic fragment]]−O−CH_2−C≡C−C≡C−[[structural formula: phenylene fragment]]−C≡C−	87.50	4.06	79.77	4.58	8.32
2. HC≡C−CH_2−O−[[structural formula: *p*,*p*′-substituted diphenylisopropylidene fragment, $C(CH_3)_2$]]−OCH−C≡CHDEB	1.0	1.0	0.38	0.08	4	1.2	yellow	[−C≡C−[[structural formula: *p*,*p*′-substituted diphenylisopropylidene fragment, $C(CH_3)_2$]]−O−CH_2−C≡C−]$_n$ [−C≡C−[[structural formula: phenylene fragment]]−C≡C−]$_m$, where n = 2, m = 1	85.71	5.49	85.30	4.51	–

Starting substances	Quantity, g	Quantity, mol	Reaction duration, h	Polymer yield, g	Polymer color	Polymer structure	Calculated, % C	Calculated, % H	Found, % C	Found, % H	Other found value, %
3. HC≡C−CH_2−O−C(O)−[[structural formula: phenyl fragment]]DEB	1.6	1.0	0.089	0.08	3	1.6	light yellow	[[structural formula: phenyl ester fragment]]−C(O)O−CH_2−C≡C− [−C≡C− [[structural formula: phenylene fragment]]−C≡C−]$_n$ −C≡C−CH_2−O−C(O)−[[structural formula: phenyl fragment]], where n = 2, ...	84.80	3.88	85.06	3.86	7.60

Starting substances	Quantity, g	Quantity, mol	Reaction duration, h	Polymer yield, g	Polymer color	Polymer structure	Calculated, % C	Calculated, % H	Found, % C	Found, % H	Other found value, %
4. $HC{\equiv}C{-}CH_2{-}O{-}$[[structural formula: hydroxyanthraquinone fragment]]DEB	1.2	0.0095	0.007	6	0.6	brown	[[structural formula: anthraquinone fragment with OH and $O{-}CH_2{-}C{\equiv}C{-}$ substituents]][$-C{\equiv}C-$ [[structural formula: phenylene fragment]]$-C{\equiv}C-]_n$ $-C{\equiv}C{-}CH_2{-}O{-}$[[structural formula: hydroxyanthraquinone fragment]], where n = 1	77.87	3.25	75.11	4.30	2.83

Starting substances	Quantity, g	Quantity, mol	Reaction duration, h	Polymer yield, g	Polymer color	Polymer structure	Calculated, % C	Calculated, % H	Found, % C	Found, % H	Other found value, %
5. $HC{\equiv}C{-}CH_2{-}O{-}$[[structural formula: phenyl fragment]]DEB	0.5	1.0	0.04	0.075	1	1.0	yellow	[[structural formula: phenoxypropargyl fragment]][$-C{\equiv}C-$ [[structural formula: phenylene fragment]] $-C{\equiv}C-]_n$ $-C{\equiv}C{-}CH_2{-}O{-}$[[structural formula: phenyl fragment]], where n = 1	87.04	4.63	81.33	4.85	4.66

Fig. 1. IR spectrum of the copolymer of dipropargyl ether of 4,4′-dihydroxydiphenyl with *p*-diethynylbenzene

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Starting substances	Quantity, g	Quantity, mol	Reaction duration, h	Polymer yield, g	Polymer color	Polymer structure	Calculated, % C	Calculated, % H	Found, % C	Found, % H	Other found value, %
6. $HC\equiv C-CH_2-O-$[[structural formula: *p*-substituted phenylene–$C(CF_3)_2$-phenylene fragment]]$-OCH_2-C\equiv CH$DEB	0.8	0.005	0.02	2	0.8	light yellow	[$-C\equiv$ formula:	80.77 = 12.58	3.10	[[structural formula:	80.68 = 9.74	3.57	

$-OCH_2-C\equiv C-]_n$ [$-C\equiv C-$[[structural formula: phenylene fragment]]$-C\equiv C-]_m$, where $n = 1$, $m = 4$

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* DEB –*p*-diethynylbenzene.

** Isolated 0.5 g of soluble polymer with melting point 160° and fluorine content 20.9%.

Fig. 1. IR spectrum of the copolymer of dipropargyl ether of 4,4′-dihydroxydiphenyl with *p*-diethynylbenzene

Fig. 2. IR spectrum of the copolymer of dipropargyl ether of 4,4′-dihydroxydiphenylol-2-propane with *p*-diethynylbenzene

Fig. 3. IR spectrum of the copolyester of propargyl ether of benzoic acid with

Fig. 2. IR spectrum of the copolymer of dipropargyl ether of 4,4′-dihydroxydiphenyl-ol-2-propane with *p*-diethynylbenzene

Figure 2: Fig. 2. IR spectrum of the copolymer of dipropargyl ether of 4,4′-dihydroxydiphenyl-ol-2-propane with *p*-diethynylbenzene

Fig. 3. IR spectrum of the copolyester of propargyl ether of benzoic acid with *p*-diethynylbenzene

Figure 3: Fig. 3. IR spectrum of the copolyester of propargyl ether of benzoic acid with *p*-diethynylbenzene

p-diethynylbenzene

Fig. 4. IR spectrum of the copolymer of dipropargyl ether of hexafluoro-2,2-bis(4-hydroxyphenyl)propane with *p*-diethynylbenzene

Depending on the ratio of the *p*-diethynylbenzene taken into the reaction, the intensities of the absorption bands characteristic of *p*-disubstituted phenyl nuclei change correspondingly. The data from the IR spectra are summarized in Table 1. At the same time, absorption bands characteristic of ether bonds appear in the polymer. On the basis of the spectral data, as well as the data of elemental analysis, it may be asserted that, as a result of the joint oxidation of *p*-diethynylbenzene with the ethers listed, polymers have been obtained that contain in their chain conjugated triple bonds alternating with ether groups.

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REFERENCES

1. A. M. Sladkov, V. V. Korshak, A. G. Makhsumov, *Izv. AN SSSR, ser. khim.*, 1963, 1343.

2. V. V. Korshak, A. M. Sladkov et al., *Izv. AN SSSR, ser. khim.*, 1963, No. 10, 1852.

3. V. I. Kasatochkin, A. M. Sladkov et al., *Izv. AN SSSR, ser. khim.*, 1963,

Fig. 4. IR spectrum of the copolymer of dipropargyl ether of hexafluoro-2,2-bis(4-hydroxyphenyl)propane with *p*-diethynylbenzene

Figure 4: Fig. 4. IR spectrum of the copolymer of dipropargyl ether of hexafluoro-2,2-bis(4-hydroxyphenyl)propane with *p*-diethynylbenzene

No. 10, 1786.

4. V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, *Vysokomolek. soed.*, 1963, No. 6, 793.

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