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Abstract

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Corresponding Member of the Academy of Sciences of the USSR V. V. KORSHAK, S. L. SOSIN, and V. P. ALEKSEEVA

ON OBTAINING NEW TYPES OF LINEAR POLYMERS BY THE POLYRECOMBINATION REACTION

In previous investigations on the study of the polyrecombination reaction it was shown (1,2) that, upon treatment with peroxides of such compounds as *n*-diisopropylbenzene, diisopropylferrocene, *n*-dichlorobenzene, *n*-xylylene dichloride, and a number of others, linear polymers are formed and, along with them, especially in the case of *n*-diisopropylbenzene, polymers with a cross-linked three-dimensional structure are obtained in considerable amount; these are usually infusible and insoluble. In the course of further investigations we studied the behavior in the polyrecombination reaction of such compounds as diphenylmethane and some of its derivatives, methyl phenylacetate, benzyl benzoate, from which previously only dimers had been obtained upon treatment with peroxides (3,10).

When these compounds and a number of others were treated, according to the method described by us (2), with tert-butyl peroxide at a ratio of 1.2 or more moles of peroxide per mole of starting compound at a temperature of 200°, we obtained polymers without any appreciable amounts of three-dimensional structures. Thus, from diphenylmethane a linear polymer was obtained in the form of a yellowish powder with m.p. 205—220°, soluble in benzene. The molecular weight of this polymer varies within the limits 10 000—900 000, depending on the molar ratio peroxide : hydrocarbon. The dependence of the molecular weight of this polymer on the viscosity of its solution in benzene is well expressed by the formula $[\eta] = 2.18 \cdot 10^{-3} M^{0.328}$.

The formation of the polymer may be represented by the following scheme:

$$(C_6H_5)_2CH_2 + R\cdot \to RH + (C_6H_5)_2\dot{C}H; \quad 2(C_6H_5)_2\dot{C}H \to HC(C_6H_5)_2CH(C_6H_5)_2 \xrightarrow{R\cdot}$$

$$\to HC(C_6H_5)_2C(C_6H_5)_2 \to HC(C_6H_5)_2C(C_6H_5)_2C(C_6H_5)_2\text{—}\ldots\text{—}CH(C_6H_5)_2, \qquad (I)$$

where R· denotes tert-butoxy and methyl radicals formed in the decomposition of the peroxide (7,8):

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \rightarrow (CH_3)_3CO\cdot + \cdot CH_3 + (CH_3)_2CO.$$

Thus, this polymer may be regarded as polydiphenylmethylene (I), previously unknown, since it had not been possible to obtain it, for example, from tetraphenylethylene under mild polymerization conditions (see (4)). By analogy with hexaphenylethane and higher fully arylated paraffins (5), it might have been expected that a polymer of the structure shown would be unstable and prone to spontaneous dissociation.

In fact, this polymer shows no signs of decomposition into free radicals in the presence of diphenylpicrylhydrazyl, and also displays considerable resistance to the action of such oxidizing agents as nitric acid and chromic mixture. It is quite probable that the stability of the polymer is connected with the fact that the first product of the polyrecombination reaction, the dimer—tetraphenylethane—is, in contrast to hexaphenylethane, a quite stable compound (5). The dissociation of tetraphenylethane and its high-molecular-weight analogs is not stimulated by the formation of stable triphenylmethyl radicals, as occurs in the case of hexaphenylethane and higher, fully arylated alkanes.

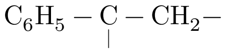
Another explanation of the stability of the polymer is connected: a) with the assumption of a rearrangement of the benzene rings, analogous to the Gomberg rearrangement (11), in the course of the reaction, which leads to the structure of poly-α,α,α'-triphenylxylylene (II), whose stability is due to the presence of phenylene-

new groups, connected in the main chain in the 1,4 position; 6) with the assumption of a rearrangement analogous to that observed by Ziegler for 1,2-dimethyltetraphenylethane (12). As applied to our case, this scheme could lead to the formation of unsymmetrical diphenylethylene and its subsequent polymerization with formation of polydiphenylethylene (III).

The composition of the elementary unit in structures (I) and (II) is the same: $C_{13}H_{10}$ (C 93.93%; H 6.07%); in structure (III) the unit composition is $C_{14}H_{12}$ (C 93.28%; H 6.72%). Actually found, %: C 93.11; H 6.96. The oxidation products of structures (I) and (III) should be identical. To decide the question of which structure should be assigned to the polymer obtained, the IR spectra were compared of polymers prepared under the same conditions from different starting compounds, namely from diphenylmethane, tetraphenylethane, tetraphenylethylene, and 1,1-diphenylethylene. In this comparison, the variant of structure (II) was immediately eliminated, since in the IR spectrum of polydiphenylmethylene there is no absorption maximum in the region 833-840 cm^{-1}, characteristic of a benzene ring substituted in the 1,4 position.

Fig. 1. Dependence of the yield of polymer and diphenylmethane dimer on the molar ratio peroxide:hydrocarbon. *I* —starting hydrocarbon; *II* —dimer; *III* —polymer.

On the other hand, these spectra of polymers obtained from diphenylmethane and tetraphenylethane have coincident absorption maxima in the region 701 and 747 cm^{-1}, characteristic of monosubstituted benzene (^{6}), but do not have a maximum in the region 760 cm^{-1}, which appears distinctly in the spectrum of the polymer from 1,1-diphenylethylene. This maximum is characteristic of the configuration



$$C_6H_5 - \underset{|}{C} - CH_2 -$$

which includes a methylene group and occurs in polymers from dibenzyl, styrene, and 1,1-diphenylethylene. Thus, on the basis of IR spectral data, the polymer obtained from diphenylmethane should be assigned structure (I)—polydiphenylmethylene.

Fig. 2. Dependence of the molecular weight of the polymer on the molar ratio peroxide:hydrocarbon. *I* —theoretical curve; *II* —experimental curve.

From the dependence presented in Fig. 1 of the yield of reaction products on the molar ratio peroxide:hydrocarbon, it is evident that the first mole of peroxide is consumed almost exclusively in the conversion of all the diphenylmethane into the dimer tetraphenylethane, the yield of which is $> 90\%$ (curve *II*). In the course of the reaction, tetraphenylethane is not converted completely into polymeric products—its yield, having decreased to 50% (at a molar ratio peroxide:hydrocarbon of 2:1), remains constant upon further addition of peroxide, as does the yield of polymer, which reaches 50% at the same ratio (curve *III*). Such stabilization of the yield of polymer and dimer is apparently associated with a change in the viscosity of the medium, which at the end of the reaction is not a solution but a viscous melt. An increase in the viscosity of the medium hinders the escape of radicals from the cage (^{13}).

It is evident from Fig. 2 that the addition of peroxide in excess of two moles per mole of diphenylmethane leads to a sharp increase in the molecular weight of the polymer (curve *II* asymptotically approaches the ordinate axis), which reaches a maximum value of 900,000 (determined by the light-scattering method).

In Fig. 2, curve *I* represents a theoretical curve of the change-

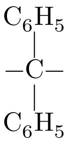
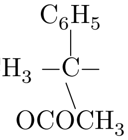
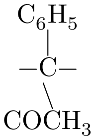
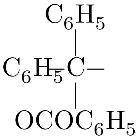
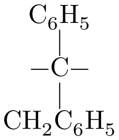
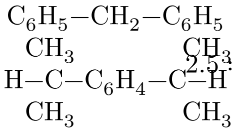
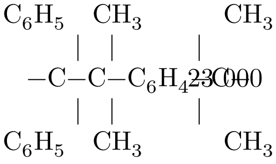
of the polymer molecular weight as a function of the molar ratio peroxide : hydrocarbon. This curve was constructed on the assumption that chain growth proceeds by doubling, i.e., a tetramer is formed from a dimer, an octamer from a tetramer, etc. Under this assumption, the number of moles of free radicals necessary for the conversion of 1 mole of hydrocarbon into a polymer of infinitely large molecular weight may be represented as: $N_R = 1 + 1/2 + 1/4 + ... + (1/2)^k$, where k is the natural series of numbers $0, 1, 2 ...$, i.e., as the sum of a geometric progression with first term $a = 1$ and ratio $q = 1/2$.

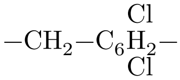
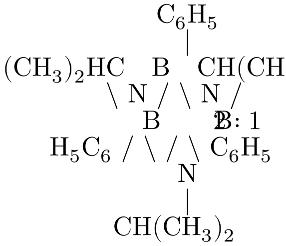
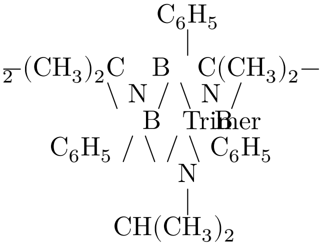
On the other hand, according to the accepted assumption, the degree of polymerization is $n = 2^{k+1}$. Hence we obtain the following relation between the number of moles of free radicals and the coefficient n: $N_R = 2 - 2/n$.

It is evident from Fig. 2 that the experimentally observed curve II has exactly the same character as the theoretical curve I and agrees with it rather closely, which confirms the assumption made concerning the nature of chain growth.

Table 1

Compounds that, in the polyrecombination reaction, give polymers of linear structure

Starting compound	Molar ratio peroxide : starting compound	Structure of the unit of the resulting linear polymer	Mol. weight	M.p., °C	Yield, % of starting compound
$C_6H_5-CH_2-C_6H_5$	2.3 : 1	 $-\overset{C_6H_5}{\underset{C_6H_5}{C}}-$	900 000	205—220	52
$C_6H_5-CH_2-C(=O)-OCH_3$	2.5 : 1	 $-\overset{C_6H_5}{\underset{OCOCH_3}{C}}-$	14 000	160—170	48
$C_6H_5-CH_2-C(=O)-CH_3$	1.8 : 1	 $-\overset{C_6H_5}{\underset{COCH_3}{C}}-$	30 000	210—220	36
$C_6H_5-CH_2-O-C(=O)-C_6H_5$	2.7 : 1	 $-\overset{C_6H_5}{\underset{OCOC_6H_5}{C}}-$	430 000	185—200	55
$C_6H_5-CH_2-CH_2-C_6H_5$	3 : 1	 $-\overset{C_6H_5}{\underset{CH_2C_6H_5}{C}}-$	5 000	170—185	70
 $C_6H_5-CH_2-C_6H_5$ $H-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_4-\overset{CH_3}{\underset{CH_3}{C}}-H$	2.5 : 1	 $-\overset{C_6H_5}{\underset{C_6H_5}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-C_6H_4-\overset{CH_3}{\underset{CH_3}{C}}-$	23 000	146—160	55

Starting compound	Molar ratio peroxide : starting compound	Structure of the unit of the resulting linear polymer	Mol. weight	M.p., °C	Yield, % of starting compound
$C_6H_4(CH_3)_2Cl_2$	2 : 1	 $-CH_2-\underset{Cl}{\overset{Cl}{C_6H_2}}-CH_2-$	1[illegible] 000	150–165	65
	2 : 1		Trimer	~200	49
ferrocene, $Fe(C_5H_5)_2$	1 : 1	ferrocene unit, $-C_5H_4-Fe-C_5H_4-$	2500	~300	16

It follows from this that, under the experimental conditions, tert-butyl peroxide decomposes in such a way that from one mole of peroxide, instead of 2 moles of radicals active with respect to the solvent (8,9), 1 mole of such radicals is formed, and, correspondingly, the maximum molecular weight is attained at a peroxide consumption close to two moles per mole of hydrocarbon. This may be explained by the fact that, under these conditions, half of the initially formed free radicals is consumed not in abstracting hydrogen atoms from the solvent, but in side reactions. In the gaseous products, by gas chromatography, we detected methane in an amount of 50% of the theoretical value. The corresponding loss of methyl radicals may be partly connected with the fact that, in addition to the decomposition of butoxy radicals into methyl radicals and acetone, these radicals react with one another to form methyl tert-butyl ether and acetone (14).

In an analogous manner, linear polymers soluble in benzene and having high molecular weight were obtained by us from the methyl ester of phenylacetic acid, the benzyl ester of benzoic acid, and other compounds shown in Table 1. In contrast to the linear polymers described, when durol, ditolylmethane, n,n'-diisopropyldiphenyl, benzyl acetate, and certain other compounds are introduced into the reaction in place of diphenylmethane, insoluble polymers are formed in considerable amounts together with linear polymers; these apparently have a cross-linked structure due to methyl groups. It is interesting to note that, by means of the polyrecombination reaction, it is possible to obtain linear polymers with aromatic rings not only in the side chain but also in the main chain. Thus, for example, by copolymerization of diphenylmethane (0.1

mole) and *n*-diisopropylbenzene (0.1 mole), on treatment of this mixture with 2.5 moles of peroxide, an exclusively linear copolymer is formed, whereas *n*-diisopropylbenzene alone, under these conditions, is converted almost entirely into a three-dimensional product (2). Under the same conditions, from 2,5-dichloro-*n*-xylene a chlorinated analog of poly-*n*-xylylene is obtained, completely soluble in benzene. Apparently, chlorine atoms in the *o*-position to the methyl groups shield them and hinder cross-linking of the linear chains through these groups.

From the data presented it follows that the polyrecombination reaction leads to the preparation of linear polymers of high molecular weight if the starting compounds do not contain groups capable of serving as branching points of the polymer chain.

If electron-accepting carbomethoxy groups are present in both benzene rings of diphenylmethane (dimethyl ester of n, n'-diphenylmethanedicarboxylic acid), then the polyrecombination reaction, in contrast to diphenylmethane, is limited only to the stage of dimer formation; this, along with other factors, may be connected with the greater difficulty of abstracting α-hydrogen atoms in the presence of electron-accepting substituents in the ring (8). A dimer of the indicated structure was isolated in 75.6% yield.

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