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STABLE POLYMERIC CARBON RADICALS, 2nd PART; ATTEMPTS AT THE PREPARATION OF POLYRADICALS OF THE TRIPHENYLMETHYL TYPE LINKED BY P-PHENYLENE UNITS

Dietrich Braun and Peter Lehmann

Translation of "Stabile Polykohlenstoffradikale, 2;Versuche zur Darstellung von Polyradikalen des Triphenylmethyl-Typs, verknupft uber p-Phenylen-Einheiten", Makromolekulare Chemie, Vol. 177, 1976, pages 1387-1400.

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16. Abstract

As starting materials for the preparation of polyradicals of triphenylmethyl type linked by p-phenylene units bis(4-iodophenylmethane (5a) and bis(4-iodo-2.5-dimethyl-phenylmethane (5b) were synthesized by a Sandmeyer reaction from the corresponding diamino compounds and subsequently transformed into t the corresponding polymeric hydrocarbons 6a and 6b by an Ullmann condensation. In the following step 6a and 6b were brominated at the tert. carbon atom by means of N-bromosuccinimide. The reaction of the resulting poly (4.4'-biphenylylen-α-bromobenzylidene)s (7a and7b) with mercury afforded the corresponding radicals, the ESR-spectra of which were recorded. From the methyl substituted polymer 7b poly/‾(2.2'5.5-tetramethyl-4.4'-bi-phenylylen)phenylmethylidyne_/ (3) was formed, whereas the unsubstituted product 7a was transformed into a para-quinoide polymer with radical properties.

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STABLE POLYMERIC CARBON RADICALS, 2nd PART[*] [**]

/1387

Attempts at the Preparation of Polyradicals of the Triphenylmethyl Type Linked by P-Phenylene Units

Dietrich Braun and Peter Lehmann

Summary:

As starting materials for the preparation of polyradicals of triphenylmethyl type linked by *p*-phenylene units bis(4-iodophenyl)phenylmethane (**5a**) and bis(4-iodo-2,5-dimethylphenyl)phenylmethane (**5b**) were synthesized by a Sandmeyer reaction from the corresponding diamino compounds and subsequently transformed into the corresponding polymeric hydrocarbons **6a** and **6b** by an Ullmann condensation. In the following step **6a** and **6b** were brominated at the tert. carbon atom by means of *N*-bromosuccinimide. The reaction of the resulting poly(4,4'-biphenylylen-α-bromobenzylidene)s (**7a** and **7b**) with mercury afforded the corresponding radicals, the ESR-spectra of which were recorded. From the methyl substituted polymer **7b** poly[(2,2',5,5'-tetramethyl-4,4'-biphenylylen)phenylmethylidyne] (**3**) was formed, whereas the unsubstituted product **7a** was transformed into a *para*-quinoide polymer with radical properties.

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1. Introduction

About 70 years ago Gomberg[1] discovered the reversible disintegration of a substance considered by him to be hexaphenylethane, into two molecules of triphenylmethyl. As a result of his and many later studies, extensive information has been gathered on the subject of radicals of low molecularity. However, up till recently, little has been known about stable macromolecular substances with unpaired electrons. It has, of course, been known for a long time that many of the formation reactions and disintegration processes of macromolecules take place according to radical mechanisms; the radicals occurring in these processes are however usually very reactive and thus quickly become further converted.

It was therefore of interest to prepare by clear chemical methods macromolecules that produce in the polymer chains many groups with unpaired electrons whose structure is determined by synthesis. By analogy with polyions, the term polyradicals[2] was proposed for

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[*] Part 1: D. Braun, W. Euler, Makromol. Chem. 177, 1373 (1976).

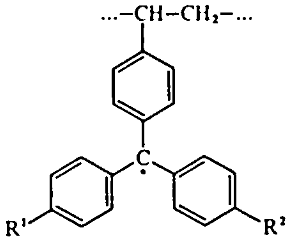
[**] By Dietrich Braun and Peter Lehmann of the German Institute For Synthetic Materials, D-6100 Darmstadt, West Germany. (Submitted on August 27, 1975).

[***] Numbers in the margin indicate foreign pagination

these macromolecules, while the designation macroradicals should be used for polymers with only one radical position, usually at the end3).

The first stable polyradicals were polyhydrazyls that were obtained by Braun et al.4). In addition to producing these and other polynitrogen radicals5,6), it has also been possible to synthesize polyoxygen radicals and polyradical ions8,9).

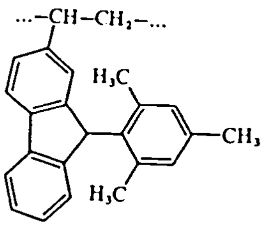
The first polycarbon radicals were produced by Braun and Faust10) and were poly-α,α-diaryl-4-vinylbenzyl radicals, poly{1-[4-(diarylmethylene)phenyl]-ethylene} e (1a-c):



1

	R^1	R^2
1 a	H	H
b	C_6H_5	C_6H_5
c	H	C_6H_5

In contrast to polynitrogen radicals, these polycarbon radicals are very sensitive to oxygen; furthermore, like the corresponding compounds of low molecularity, the polytriarylmethyl radicals, which are relatively stable under inert conditions, are in equilibrium with their dimers; this produces fairly heavily cross-linked polymers. Therefore Braun and Euler11) tried to synthesize polycarbon /1389 radicals in which, based on the behavior of their low molecular model, no or only slight cross-linking could be expected, particularly as a result of steric hindrance. Poly(2-vinyl-9-mesityl-9-fluorenyl)*) proved to become dissociated up to 100% and thus fully accessible without cross-linking (2).



2

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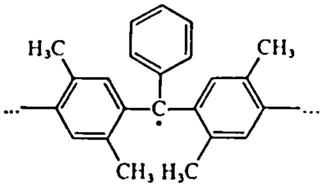
*)poly{1-[2-(9-mesityl-9-yl)(fluorenyl]ethylene}.

With all the polyradicals mentioned up to now, the macromolecular structure was produced by polymerization of a vinyl compound; the radical points were subsequently introduced by chemical conversion in the polymer. All the polyradicals mentioned produce the radical points as substitutions in the main chain.

It therefore seemed natural to try to produce polyradicals whose radical points occur only in the main chain. The synthesis of these "main chain polycarbon radicals" is made more difficult by the fact that both the intermolecular and intramolecular combination of free electrons in adjacent radical positions must be prevented as much as possible.

After studying Tschitschibabin hydrocarbon and its derivatives, we found possibilities for structural arrangements in which no significant linkage can take place between the unpaired electrons of adjacent radical points. An effective isolation of radical centers /1390 occurs if several saturated aliphatic carbon atoms are interposed between them[12)], if the radical points are linked in the meta-position by aromatic rings[13)] or if the reciprocal action of the free electrons is avoided by means of disturbance of the level position[14)].

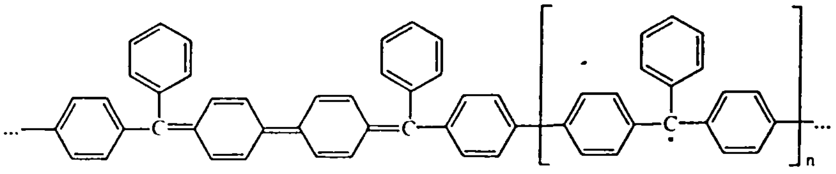
Having considered these viewpoints, we attempted the synthesis of poly[(2,2',5,5'-tetramethyl-4,4'-biphenylylene)-phenylmethylidine] (3).



3

We anticipated that steric hindrance by two methyl groups in the 5 positions prevents the linking of adjacent free electrons and that shielding the unpaired electrons by the two methyl groups in the 2 positions avoids intermolecular combination.

In addition, we tried to achieve the synthesis of the corresponding unsubstituted polymer, since it would be possible to form here on the one hand a macroradical 4a (if an uneven number of adjacent bromide atoms are split off) and, on the other hand, a polymeric quinoidal system, a "poly-Tschitschibabin hydrocarbon" 4b (if an even number of adjacent bromide atoms are split off).



	n
4a	0
b	1

4

The macroradical 4a differs from the "poly-Tschitschibabin hydrocarbon" 4b only by one additional radical point.

Two principle methods of preparing these polymers came to mind:

1. Linking triphenylmethyl units, forming biphenylylene groups.
2. Synthesis of a polyketone and building the carbon structure of the later polyradical foundation stone by means of conversion with an organic metal compound.

The method of synthesis via a polyketone was not chosen, since for this, the number of polymer-analog conversions required was higher than in the case of the linking of triphenylmethyl units.

2. General section

/1391

2.1 Bis(4-iodophenyl)phenylmethane (5a) and bis(4-iodo-2,5-dimethylphenyl)phenylmethane (5b).

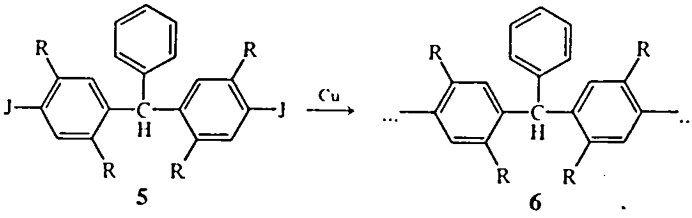
The starting material for the preparation of bis(4-iodophenyl)-phenylmethane (5a) was bis(4-aminophenyl)phenylmethane, which was obtained by condensation of aniline with benzaldehyde at approx. 150°C[15]. Bis(4-aminophenyl)-phenylmethane was diazotized in diluted sulphuric acid at 0°C by the addition of sodium nitrite solution and then poured rapidly, since the diazonium salt disintegrates, into a KI/I_2 solution. 5a was obtained from the tarry product after extensive cleaning operations in the form of a small light orange crystal.

Bis(4-iodo-2,5-dimethylphenyl)phenylmethane (5b) was synthesized according to directions by Ullmann[17] by diazotization of bis(4-amino-2,5-dimethylphenyl)phenylmethane[16] and conversion with hydriodic acid. The diamino compound was obtained by condensation of p-xylidine and benzaldehyde.

The constitution of 5a and 5b was verified by IR, UV and NMR spectroscopy as well as by analysis.

2.2 Ullmann polycondensation of 5a and 5b

The Ullmann reaction has been known for a long time as a method of preparing oligophenylenes. More recently it has been used by Kern et al.[18)] in order to prepare oligophenylenes from 4,4'-diiodobiphenyl. In the hope that this method can also be used for 5a and 5b, the condensation was carried out under entirely analogous conditions.



	R
5a,6a	H
b	CH_3

The average molecular weights ($\bar{M}$) determined by vapor pressure osmometrics and the average polycondensation levels ($\bar{P}$) are $\bar{M}$ = 3970 and $\bar{P}$ = 15 for poly(4,4'-biphenylylenebenzylidene) (6a) and /1392 $\bar{M}$ = 2300 and $\bar{P}$ = 7 for poly[2,2',5,5'-tetramethyl-4,4'-biphenylylene)benzylidene] 6b).

The UV spectrum of 6a (in chloroform) shows a maximum at 274 nm (ε = 15000 l mol^{-1} cm^{-1}), which is caused by the biphenyl systems formed in the condensation. In the case of methyl-substituted polyhydrocarbon, a maximum is reached at 272.5 nm; however, with ε = 4200 l mol^{-1} cm^{-1}, this demonstrates a much lower absorption coefficient, since a planar position of the two phenyl rings in the biphenyl system is greatly hindered sterically.

In the NMR spectrum for 6b, in addition to the expected signals for the aromatic protons and the protons of the C--H and CH_3 groups, a peak is also visible at τ = 6.73 ppm that corresponds to the protons of the Ar--CH_2--Ar group. The occurrence of this peak is understandable if one considers that a transfer reaction has taken place according to the following scheme:

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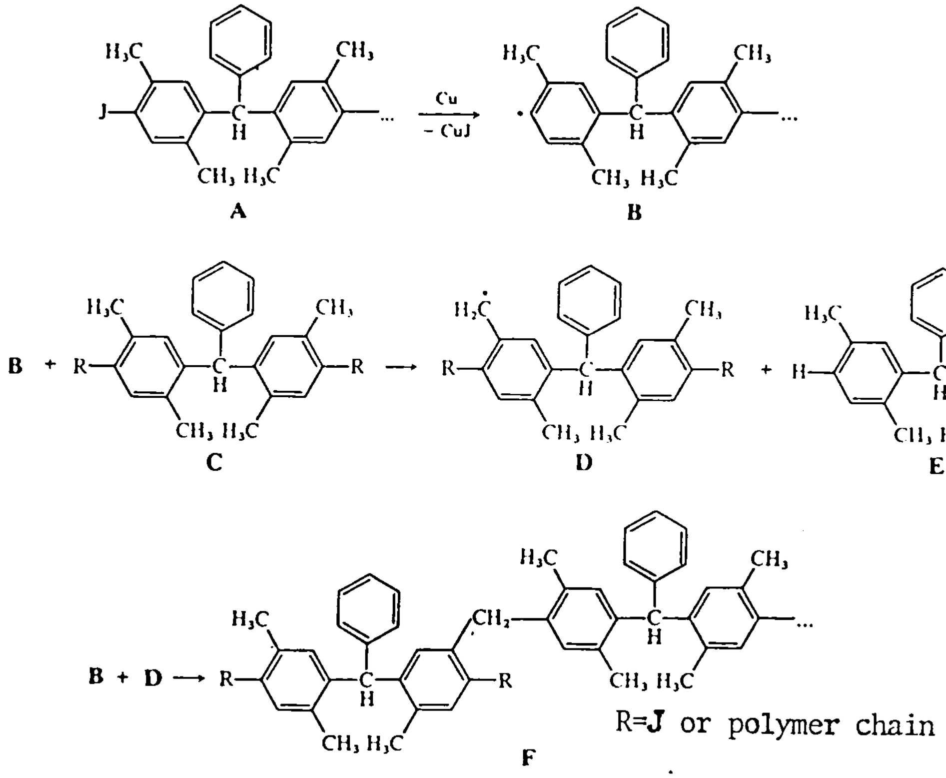


Naturally an abstraction of the hydrogen atom on the central /1393 aliphatic carbon atom is also conceivable; however, it appears to be very well protected by the methyl groups.

2.3 Bromination of 6a and 6b

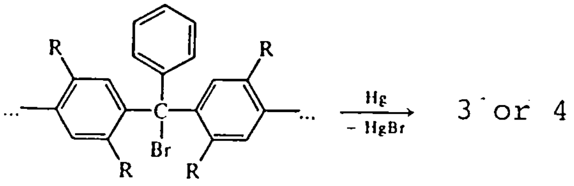
The polyhydrocarbons 6a and 6b were converted in dry carbon tetrachloride by means of N-bromosuccinimide into the corresponding bromomethane derivatives. The process of bromination could be followed easily by NMR spectroscopy. Thus the spectrum of poly-(4,4'-biphenylylene-α-bromobenzylidene (7a) showed only signals in the range of τ = 2-3 ppm which were caused by the aromatic protons. Since no peak occurs at τ = 4.53 ppm (at this point the aliphatic C--H group of 6a is absorbed), bromination has essentially occurred quantitatively.

The NMR spectrum of poly[(2,2',5,5'-tetramethyl-4,4'-biphenylylene)-α-bromobenzylidene] (7b) shows signals at τ = 2.82, 3.07 and

3.34 ppm and also at τ = 7.88 and 8.10, which correspond to the aliphatic C--H and the CH_3 groups. Peaks also appear at τ = 4.32, 5.74 and 6.49 ppm. The signal at τ = 4.32 corresponds to the central C--H group; this proves that the bromination has not taken place quantitatively at this point. The peak at τ = 6.49 ppm is caused by the Ar--CH_2--Ar group already mentioned (cf. section 2.2). The signal at τ = 5.74 ppm is wide and weak. It occurs in the ranges given in the literature [19)] for CHX and for CH_2X (X = halogen) and indicates that CH_2 groups and possibly even CH_3 groups are also brominated.

3. Preparation and detection of the radicals

Radicals were produced using mercury by separation of the bromine from the polymers 7a and 7b dissolved in benzene. Extreme care had to be taken to exclude oxygen and moisture. Radicals were /1394 produced from both polymers and their ESR spectra were recorded.



7a: R = H
b: R = CH_3

The benzene solution of 3 is yellow, which was to be expected, since the ortho-constant methyl groups isolate the individual radical points by twisting the phenyl nuclei of the biphenylylene units and the latter therefore demonstrate the same conjugation system as free triphenylmethyl.

The ESR spectrum (Fig. 1) of the radical prepared from 7b has a width of 27.5 Gauss. On the basis of this value (for radicals of low molecularity similar widths were obtained) and the twisting of the phenyl nuclei, seen in the UV spectra, by steric hind-

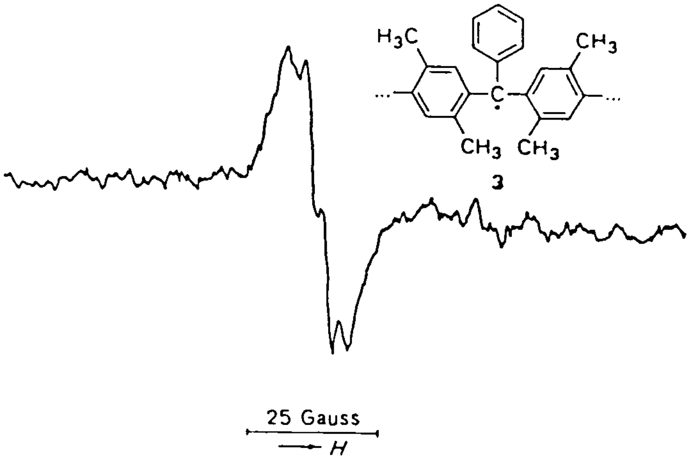
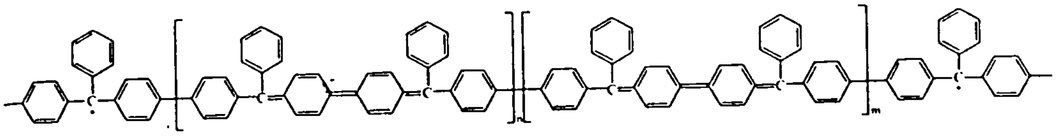


Fig. 1. ESR spectrum of poly[(2,2',5,5'-tetramethyl-4,4'-biphenylylene)-phenylmethylidine] (3) in benzene (1 Gauss = 10^{-4} Vs m^{-2})

rance, it may be very likely that in this case a polyradical is present with radical points corresponding to the structure 3. In addition to these radical points, however, there may also be others present that have been produced from the polymer F and in which one or more CH_3 groups are replaced by CH_2--Ar groups.

The benzene solution of the radical produced from 7a is deep blue in a thick layer and greenish-blue in a thinner layer, because para-quinoidal structures may form in this polymer by combination with free electrons. As long as an even number of adjacent bromine atoms are separated, a type 4a macromolecule is produced, of which the basic component is representative of the "Tschitschibabin hydrocarbons". If an uneven number of adjacent bromine atoms are dissociated, then a "poly-Tschitschibabin hydrocarbon" of type 4b is formed which, /1395
however, contains one more triphenylmethyl radical point, since each time only two molecules can combine intramolecularly.

The ESR spectrum (Fig. 2) of the radical prepared from 7a is about 29 Gauss wide. The type of radical present cannot yet be determined exactly. We are inclined to the opinion that, on the one hand, the previously mentioned "poly-Tschitschibabin hydrocarbon" may be present with one triphenylmethyl radical point and, on the other hand, as a result of twisting of biphenyl groups, a biradical of the following type might have been produced from the quinoidal macromolecule:



Finally it should be mentioned that the object of this study, i.e. to build a polyradical with precisely defined radical points in the main chain, was not entirely achieved, since, in using methyl-substituted triphenylmethanes, side-reactions occurred at two points in the synthesis process. Nevertheless it is clear that the construction principle that we chose for main chain polyradicals has prospects of success insofar as the side-reactions can be avoided. /1396 This opinion is supported particularly by the fact that no side-reactions occurred in the experiments with unsubstituted triphenylmethanes.

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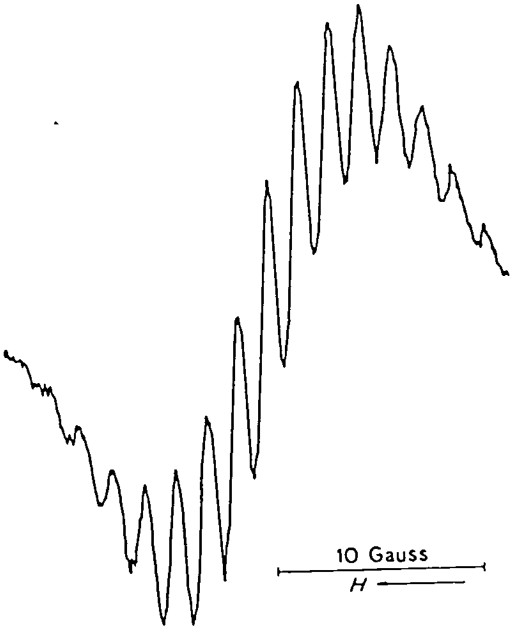

Fig. 2. ESR spectrum of the radical formed from poly(4,4'-biphenylylene-α-bromobenzylidene) (7a) in benzene.

4. Experimental section

4.1. Chemicals and solvents

Benzene was heated once to boiling over sodium in a closed apparatus in pure dry nitrogen and recovered by fractional distillation. This purified benzene was then heated to boiling for several days in nitrogen over potassium at the reflux. When the benzene became deep blue when benzophenone was added, it was suitable for use as a solvent for radicals; it was then distilled in pure dry nitrogen directly into the reaction container.

Ether was first pre-dried with $CaCl_2$ or KOH and then freed of water and peroxides with sodium wire.

Aniline and *biphenyl* were distilled before use in vacuo.

Venus copper[*] is activated[20] by stirring 20 g of copper powder in 200 ml of a 2% solution of iodine in acetone for 5 to 10 minutes. A grey product results (CuI) which is sucked off and stirred with 100 ml of a 1:1 mixture of conc. hydrochloric acid and acetone. The CuI dissolves. The residue is sucked off, flushed with acetone and dried in a vacuum dryer.

Nitrogen: Nitrogen from a cylinder was supplied via a BTS contact (BASF), silica gel and phosphorus pentoxide for the elimination of oxygen and moisture.

4.2. Preparation of the starting materials

4.2.1.1. *Bis(4-aminophenyl)phenylmethane*: 48.0 g (0.453 moles) of benzaldehyde (purest form, Merck) are heated to 150 °C with 400 g (4.3 moles) of freshly distilled aniline and 8.00 g (0.07 moles) of finely powdered aniline hydrochloride in an open 1 liter three-necked beaker with stirrer and thermometer. This temperature is maintained for 45 min; then the mixture is allowed to cool to room temperature. Thick, heavily overgrown crystals are precipitated which are suctioned off and thoroughly washed with water and then with 50% aqueous ethanol. The remaining, slightly yellow crystals are recrystallized from ethanol. Colorless crystals with a melting point of 126°C. Yield 92.6 g (56.5%). (Reference[15]: yield 144 g (87.8%)).

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[*] From the Venus Company, Nuernberg.

Since these crystals still contain 1 mole of crystalline aniline, they are mixed with 265 g of KOH (42.5%) and subjected to water vapor distillation until fresh condensate with lye shows no further turbidity. The melted residue is allowed to cool in the distillation flask, it is coarsely crushed and washed with water until a neutral reaction occurs and then dried. The dried light brown crystal mass /1397 is recrystallized from ether with the addition of activated charcoal Small colorless crystals are precipitated with a melting point of 138-139°C (Reference[15]: melting point 139°C); yield 51.4 g (73.4%) (Ref. [15]: yield 87.5%).

4.2.1.2. Bis(4-amino-2,5-dimethylphenyl)phenylmethane: 80.0 g (0.755 moles) of benzaldehyde (purest form, Merck) and 200 g (1.655 moles) of p-xylidine are heated for 6 h in 1 liter of alcoholic hydrochloric acid (prepared by saturating ethanol with HCl gas) in a reflux condenser. Then water and diluted sulphuric acid are added and the non-converted benzaldehyde is distilled off with water vapor. Alkalinity is obtained by the addition of lye and any p-xylidine still present is removed by water vapor. The residual product remains crystalline. It is flushed with water and recrystallized from alcohol. Colorless crystals; yield 195.8 g (78.5%) (ref. [16]: yield 72.4%).

4.2.2.1. Bis(4-iodophenyl)phenylmethane (5a): 51.4 g (0.189 moles) of pure bis(4-aminophenyl)phenylmethane are dissolved in 47.8 g (0.2 moles) of conc. sulphuric acid and 100 ml of water by boiling. This solution is cooled rapidly by shaking. Into the suspension obtained in this way is allowed to run slowly at 0°C a solution of 26.2 g (0.38 moles) of sodium nitrite in 40 ml of water. Since the dissolved diazonium salt even at 0°C immediately begins to disintegrate, with N_2 dissociation and substance precipitation, the normally customary filtration is dispensed with; 2-3 g of urea are quickly added to eliminate nitrous acid and 41.0 g (0.4 moles) of conc. Sulfuric acid in 40 ml of water are added. The diazonium salt solution is then quickly poured into a solution of 69.0 g of potassium iodide and 106 g of iodine (0.418 moles) in 175 ml of water. A brownish-red substance is precipitated while considerable amounts of nitrogen form. In the course of the reaction, the mixture becomes completely black as a result of precipitating iodine. It is allowed to stand overnight and is then heated by introducing water vapor until no further nitrogen formation is observed. At this point the reaction product is a sticky black substance very reminiscent of tar. Cleaning it begins by boiling the substance five times with sodium thiosulphate and with soda lye. The residue, which is still black, is dissolved in ether and then extracted five times with thiosulphate solution. It is again flushed with water and the wet ether solution is dried overnight with calcium chloride. On the following day the drying agent is filtered off and the solvent removed in a rotating vaporizer.

A dark-brown to black oil remains which cannot be caused to crystallize either by cooling or by stirring with a sharp-edged glass rod. It dissolves readily in methanol, ethanol or acetone; however, it is also not possible to recrystallize it by rectification, since again no crystals form when it cools. This oil is now mixed with A-carbon granulate and boiled five times with petroleum ether. The petroleum ether extracts obtained by filtration from the sticky black residue are recombined and concentrated in a rotating vaporizer. After the petroleum ether has been largely removed in vacuo at 60°C, a reddish-brown oil remains. By cooling it and stirring with glass rod it possible to crystallize this oil. Now these orange-colored crystals with a melting point of $\approx$65-90°C are recrystallized once from 95% aqueous acetone and twice from pure acetone. Yield 9.0 g (9.6%) of small light-orange crystals; melting point 138-140°C.

$C_{19}H_{14}J_2$ (495.9) Calc. I 51.18 /1398
Actual I 49.72

4.2.2.2. Bis(4-iodo-2,5-dimethylphenyl)phenylmethane (5b):

In analogy with Ullmann's directions[17], 66.0 g (0.2 moles) of bis-(4-amino-2,5-dimethylphenyl)phenylmethane are dissolved by heating in 100 g (2 moles) of conc. sulfuric acid and 200 ml of water and then rapidly cooled. At -5°C, 27.6 g (0.4 moles) of sodium nitrite in 50 ml of water are added. The resulting solution of diazonium salt is quickly mixed with 2.0 g of urea and poured into 250 ml (approx. 2 moles) of hydriodic acid. Strong foaming results from the formation of oxygen and a brownish-red, later dark-brown, precipitate forms. The reaction mixture is left overnight and is heated the next day until no further oxygen develops. Then solid sodium sulfite is added to the still warm suspension while it is stirred and this causes the the color of the precipitate to become noticeably lighter. A light-brown granular substance remains which is immediately absorbed in ether. The ether solution is extracted eight times each with diluted sulphuric acid and diluted caustic soda and is finally flushed with water untill neutral. After being dried with calcium chloride overnight, and the solvent has been filtered out and vaporized in a rotating vaporizer, a light-brown crystal mass remains. The crystals are precipitated when the solvent is concentrated; they are recrystallized four times from acetone with A-carbon added and are then faintly orange-yellow. Yield 16.5 g (14.5%; melting point 159-161°C).

$C_{23}H_{22}J_2$	(552.23)	Calc. I	45.96
		Actual I	45.91

4.3 Ullmann polycondensations

4.3.1 <u>Poly(4,4'-biphenylylenebenzylidene</u> (6a): 6.0 g (12.1 mmoles) of bis(4-iodophenyl)phenylmethane (5a) and 6.0 g (96 mmoles) of activated Venus copper are mixed with 15 g (97 mmoles) of distilled biphenyl. This mixture is placed in the reaction container which consists of a glass tube about 3 mm thick, is closed at the bottom and has at the top a NS 29 sleeve. Slightly below the NS 29 sleeve is an attachment with a NS 14.5 sleeve. A ground glass stirrer is fastened in the 14.5 sleeve that is suitable for stirring highly viscous substances. Into the NS 14.5 sleeve is set a stopcock with an NS 14.5 ground glass core; later nitrogen is introduced through this stopcock.

After the reaction container is filled with the mixture substance, approximately 0.5 g of mercury are added, the stirrer is set in place and evacuation is carried out. Now it is filled with nitrogen and evacuated again. It is then refilled with nitrogen and the mixture is heated in an oil bath to 190°C. After the mixture has melted.

ed, it is slowly stirred (30-60 rotations per min); there is a slight excess pressure of nitrogen. In about 4 h the mixture is heated to 225°C and this temperature is held for a further 16 h. At the end of this time an equal bulk volume of aluminum oxide is added, it is stirred somewhat and then cooled. The reaction product, which can easily be removed from the reaction container by means of the aluminum oxide, is transferred to an extraction sleeve and extracted with 250 ml of benzene in a Soxhlet apparatus. The polymer is obtained by instilling the benzene solution into excess methanol. It is twice precipitated by rectification and then dried in a vacuum drying cupboard at 50°C. Light-brown substance; yield 0.7 g (23.9%). /1399

4.3.2. Poly[(2,2',5,5'-tetramethyl-4,4'-biphenylylene)benzylidene] (6b): 14 g (0.0254 moles) of bis(4-iodo-2,5-dimethylphenyl)phenylmethane (5b) and 14 g (0.22 moles) of activated Venus copper were mixed in 35 g (0.21 moles) of distilled biphenyl. Synthesis and preparation were carried out in exactly the same way as in the case of 6a. Light-orange substance; yield 6.5 g (84.4%).

4.4. Bromination of polyhydrocarbons

4.4.1. Poly(4,4'-biphenylylene-α-bromobenzylidene) (7a): 0.53 g (2.2 moles) of poly(4,4'-biphenylylenebenzylidene)(6a) are carefully heated while being stirred in 30 ml of dry carbon tetrachloride with 0.43 g (2.42 mmoles) of N-bromosuccinimide in a 50 ml three-necked flask. The reaction mixture is heated to boiling for 3 h under reflux, and it becomes dark in color. Then it is filtered off and the brominated polymer is precipitated by instillation into dry petroleum ether. After three re-precipitations from carbon tetrachloride into petroleum ether the polymer can be used for preparing the radical. Blue polymer; yield 0.25 g (35.4%).

4.4.2. Poly[2,2',5,5'-tetramethyl-4,4'-biphenylylene)-α bromobenzylidene] (7b): 4.00 g (13.1 mmoles) of poly[2,2',5,5'-tetramethyl-4,4'-biphenylylene)benzylidene](6b) are brominated in 50 ml of dry carbon tetrachloride with 2.45 g (13.6 mmoles). In addition, 50 mg (0.3 mmoles) of 2,2'-azoisobutyronitrile are added and the reaction time increased to 7 h. This preparation corresponds to the method given in 4.4.1. Light-purple polymer; yield 2.2 g (56%).

4.5. Preparation of radicals

A magnetic stirring core was placed in a swinging tube fitted with a frit and an ESR test tube. Then the apparauts was heated intensively three times at 10^{-2} mbar and each time filled with purest dry nitrogen. Then 50 mg of the substance and 0.5 g of mercury purified with phosphorus pentoxide and aluminum oxide[21)] were poured into the swinging tube while nitrogen flowed in. After that, 25 ml of benzene were distilled directly from the ketyl solution into the mixture. The swinging tube was sealed and frozen in a dry ice/methylene chloride cooling bath. Then evacuation was carried out again, it was thawed in vacuo and filled with nitrogen. This procedure was then repeated once again. Next the mixture was stirred intensively for 1 h. Finally the solution of polyradicals was filtered through the frit into the ESR test tube.

The ESR spectrum was recorded immediately.

4.6 ESR spectra

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The spectrum of the radical from poly(4,4'-biphenylylene-α-bromobenzylidene) (7a) was recorded on an AEG electron resonance spectrometer 12 X.

A Varian EPR spectrometer V 4500-10 was used to record the ESR spectrum of poly[(2,2',5,5,-tetramethyl-4,4'-biphenylylene)phenylmethylidine] (3).

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