POLYMERIZATION OF ARYLDIAZOALKANES

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INTRODUCTION

The polymerization of aryldiazoalkanes has been examined on the basis of two reaction possibilities. When the aromatic ring carries an adequate substituent, *polyaddition* with nitrogen-evolution can occur following the reaction

$$n\,\mathrm{HX{-}Ar{-}\overset{\overset{\displaystyle R}{|}}{C}N_2} \longrightarrow n\,\mathrm{N_2} + \mathrm{{-}(X{-}Ar{-}\overset{\overset{\displaystyle R}{|}}{C}H{-})}_n \quad (\mathrm{R} = \mathrm{H,\ alkyl,\ aryl})$$

In this case aromatic rings would be included in the main chain and a polybenzylether or thioether should be formed starting from an hydroxy- or thiolaryldiazoalkane, respectively. On the other hand, if the aryldiazoalkane is unsubstituted, or if the substituent is unreactive towards the diazoalkane group or its decomposition product, *polymerization* can proceed with nitrogen evolution and the formation of polyarylidenes.

$$n\,\mathrm{X{-}Ar{-}CHN_2} \longrightarrow n\,\mathrm{N_2} + \mathrm{(\underset{\underset{\displaystyle ArX}{|}}{{-}CH{-}})}_n$$

The aromatic groups are then present as side groups along the polymeric back-bone. Such a type of polymerization of diazoalkane has already been described by several authors, particularly by Bawn, Ledwith and coworkers[1-7] in the case of their decomposition in the presence of a Lewis acid as boron trifluoride; it was assumed that the reaction proceeds through a pseudo-cationic mechanism[3]. On the other hand, Nasini and coworkers also prepared some polyalkylidenes by decomposition of diazoalkanes in heterogeneous systems on colloidal metal surfaces, e.g. colloidal gold[8-15]; in this case, however, carbene intermediates were postulated by the authors[12, 14, 15].

From an organic point of view these polyarylidenesc an be compared with the polymers of general formula

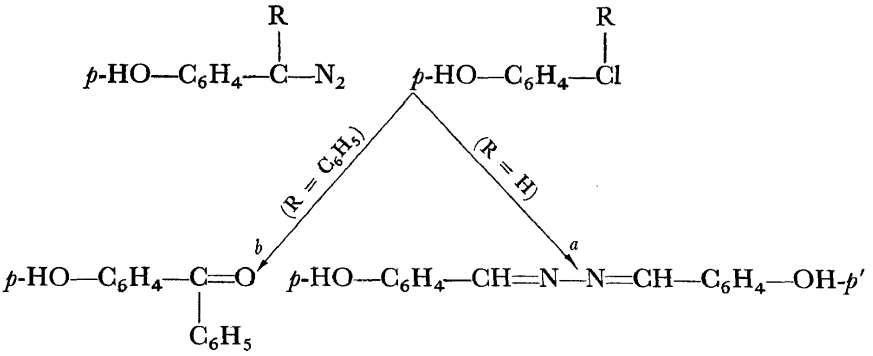
$$\mathrm{{-}\overset{\overset{\displaystyle X}{|}}{\underset{\underset{\displaystyle Ar}{|}}{C}}{-}} \quad (\mathrm{X\ is\ OBz,\ OAc,\ CO_2Me,\ COMe,\ CH_2Ph,\ Ph,\ etc.})$$

obtained by Korshak *et al.*[16, 17] by polyrecombination reaction, i.e. dehydropolymerization of the corresponding aromatic derivatives in the presence of large amounts of peroxides; in these polymers, every carbon atom of the

main chain is, however, disubstituted. In this lecture we will consider successively the two reaction possibilities.

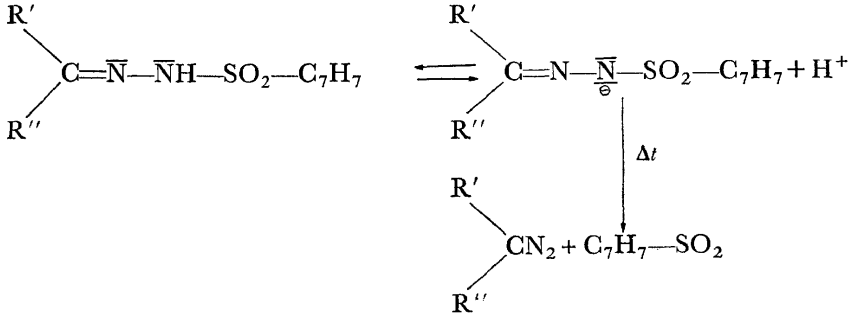
POLYADDITION†

The first approach of polyaddition was based upon the formation of *p*-hydroxy-phenyldiazomethane by mercuric oxide oxidation of *p*-hydroxy-arylhydrazones following the method of Curtius[18] and Staudinger[19]. The reactions were carried out in different solvents (benzene, diethyl ether, alcohol), in the presence or absence of an alkaline catalyst[20]; only *p,p'*-dihydroxy-benzalazine was obtained by reaction of the carbene with undecomposed diazo-derivative (reaction *a*)



The HgO-oxidation of *p*-hydroxy-benzophenone hydrazone proceeds only in alkaline medium; *p*-hydroxyphenyl-phenyldiazomethane undergoes a nice first order decomposition reaction ($k_1 = 1{\cdot}7 \times 10^{-4}\ \mathrm{sec}^{-1}$). However, it gives mainly *p*-hydroxy-benzophenone (path *b*) on account of the oxidation of the carbene in agreement with the results of Kirmse, Horner and Hoffman[21]; as expected, in the alkaline medium no self alkylation products can be obtained.

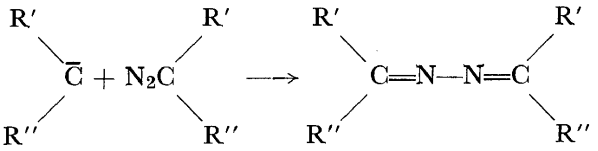
The second method of polyaddition was based upon the decomposition of tosylhydrazones of *p*-hydroxy- or *p*-thiol-aldehydes or ketones in alkaline medium with formation of diazoalkanes, following the procedure of Bamford and Stevens[22]



† In collaboration with Dr W. Bracke.

This method is well known for the preparation of the diazoalkanes when R′ and R″ stabilize them[23–25]; more often the diazoalkanes are decomposed directly in the reaction mixture, e.g. in aprotic medium with the formation of carbenes, so that the method is successfully applied to the study of the reaction of carbenes[26–30].

In the presence of an excess of sodium methoxide in aprotic medium the diazoalkane decomposes in the corresponding carbene, giving mainly azine as the reaction product



If, however, the amount of base is less than the stoichiometric quantity of tosylhydrazone, the diazoalkane can decompose with any acid present in the reaction medium, and alkylation of these acids becomes possible. As far as we know, this reaction has not yet been examined for alkylating directly with diazoalkanes; it is, however, this condensation principle that was used in the present work for polyaddition purposes starting from a *N*-tosyl-, oxy-, or mercapto-benzalhydrazone.

In these condensations, besides sodium *p*-tosylsulphinate $C_7H_7SO_2Na$ formed by thermal decomposition of sodium salt of the tosylhydrazone three different acidic hydrogens can be present in the reaction medium, namely the *N*-hydrogen of the tosylhydrazone, that of a phenol and (or) that of a mercaptan group. Their pK-values are given in *Table 1*, as well

Table 1. Alkylation of acids with aryldiazomethane

Acid	pK	*Alkylation product*
Tos—NH—N=CH—Ar	7·1	Tos—N(CH$_2$Ar)—N=CH—Ar
Ar′—OH	10·0	Ar—CH$_2$—O—Ar′
Ar′—SH	8·3	Ar—CH$_2$—S—Ar′

as their alkylation products being respectively a *N*-benzyl substituted derivative, a benzylaryl-ether or thio-ether.

Several cross-reactions were carried out in order to check the relative reactivity of the different species (see *Figure 1*). The decomposition of 1 mole *p*-methoxy-benzal tosylhydrazone with 1·2 mole base in pyridine solution (reaction scheme *a*) in the presence of 1·2 mole phenol gives only *N*-substitution, besides some azine; contrarily with 1·2 mole thiophenol, *p*-methoxy-benzyl-thioether is formed.

This striking difference of behaviour between phenol and thiophenol is also confirmed by similar experiments with *p*-hydroxy-benzal tosylhydrazone (scheme *b*). One more difference is found here, namely the influence of the solvent on the nature of the reaction product, *N*-substitution occurring in

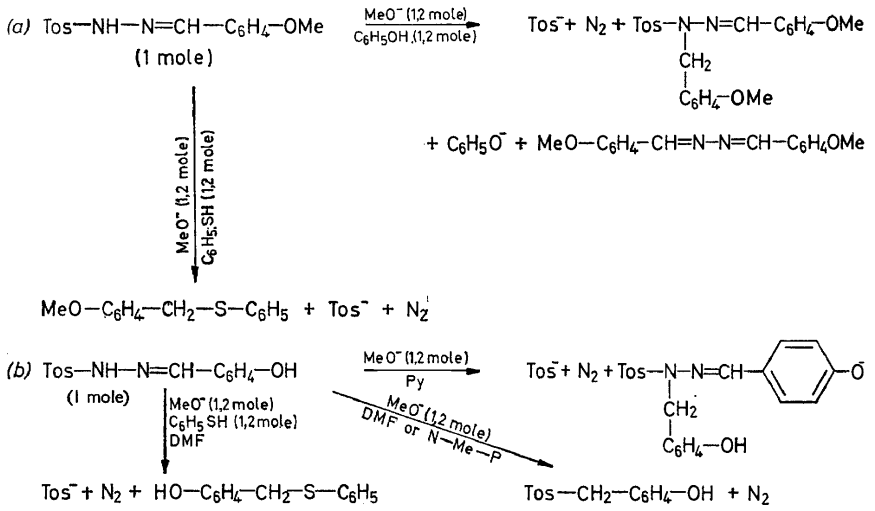


Figure 1. Cross-alkylation reactions with aryldiazoalkanes

pyridine medium, while sulphone formation in dimethylformamide (DMF) or *N*-methylpyrrolidone (N—Me—P). This influence can be interpreted assuming a tautomerism between *p*-hydroxyphenyl-carbene and *p*-quinone

$$HO—C_6H_4—CH^- \rightleftarrows O{=}C_6H_4{=}CH_2$$

methide and will be discussed elsewhere.

From these experiments it may be concluded that the alkylation reaction is not governed by the acidity of the reactants but by their nucleophilic character, the order of reactivity being

$$Ph—S^- > Tos—\bar{N}—N{=}CH— > Ph—O^- > Ph—SO_2^-$$

while the base strengths are classified

$$Ph—O^- > Ph—S^- > Tos—\bar{N}—N{=}CH— > PhSO_2^-.$$

The same order of nucleophilicity was found in competition reactions of benzyl chloride towards these anions in solution (see *Figure 2*). From these

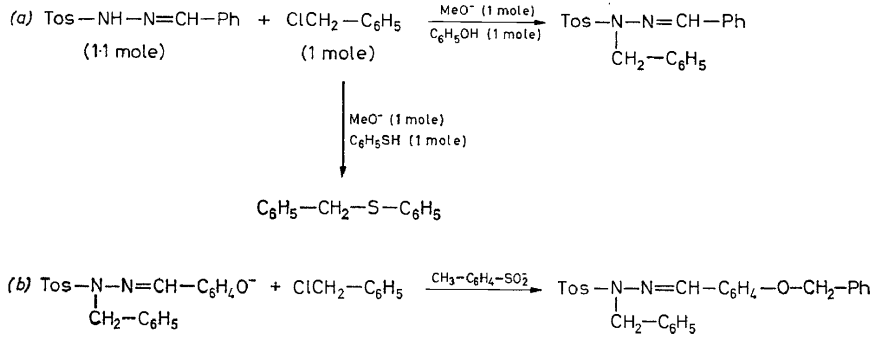


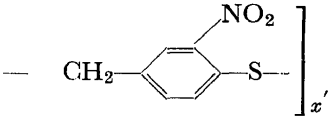
Figure 2. Alkylation reactions with benzylchloride

experimental data, it results that polymer formation should succeed by thermal decomposition of *N*-tosyl-*p*-mercapto-benzalhydrazone with sodium methoxide in dimethylformamide solution, the reaction scheme being:

$$\mathrm{Tos{-}NH{-}N{=}CH{-}C_6H_4{-}SH} + \mathrm{N_2CH{-}C_6H_4{-}SH} \longrightarrow$$
$$\mathrm{Tos{-}NH{-}N{=}CH{-}C_6H_4{-}S{-}CH_2{-}C_6H_4{-}SH} + \mathrm{N_2} \longrightarrow$$
$$\mathrm{N_2CH{-}C_6H_4{-}S{-}CH_2{-}C_6H_4{-}SH} \longrightarrow \mathrm{-[CH_2{-}C_6H_4{-}S{-}]}_x$$

Indeed polymers were obtained in dimethylformamide and in pyridine solutions of which the molecular weights were 2900 ($x = 23$–24) and 2160 ($x = 18$), respectively. As shown by infrared absorption band at 1620 cm^{-1}, some azine links are always formed followed by a decrease in the ratio diazoalkane/mercaptan, and consequently a relatively low molecular weight.

Similarly, a poly-3-nitro-4-thioether has been obtained ($x = 19$) starting from the *N*-tosyl-3 nitro-4-mercapto-benzalhydrazone



As conclusion, the polyaddition reaction of diazoalkane is governed by the nucleophilic character of the substituent, and polybenzyl thioether can be prepared in which the aromatic rings are included in the back-bone of the polymers.

POLYMERIZATION†

When benzaltosylhydrazone is decomposed at 80°C in a heterogeneous system ethylene glycol–benzene (1:1) in the presence of 2·5 equivalent of sodium glycolate, 25 per cent polybenzylidene is obtained, besides about 44 per cent monobenzyl glycol ether, 12 per cent *trans*-stilbene and 9 per cent azine. The polymer obtained corresponds to $\mathrm{-[CH(C_6H_5)-]}_x$, as shown by elemental analysis and its infrared spectrum; it is very similar to the polymer obtained in the presence of boron trifluoride (*Figure 3*). These results differ markedly from the data of Nozaki and coworkers[28] who examined the thermal and photochemical decomposition of benzaltosylhydrazone in the presence of sodium methoxide in various solvents (benzene, cyclohexane, dimethylformamide); they isolated *N*-benzylbenzal tosylhydrazone, sulphone, stilbene and azine, but no polymer.

The optimum reaction conditions for the polymerization reactions are the following: reflux till decoloration of a heterogeneous mixture of water–methanol–benzene in a volume ratio 4:1:5, containing 10 mmole tosylhydrazone and 25 mmole sodium hydroxide for 100 ml total volume; in such conditions, 85 per cent polymer is obtained besides 10 per cent azine and some *trans*-stilbene. In these reactions, the presence of an alcohol is necessary, although its nature is of secondary importance; indeed the reaction proceeds with similar high yields of polymer (75–85 per cent) and similar degrees of polymerization, when ethanol or isopropanol is used

† In collaboration with J. Hermans.

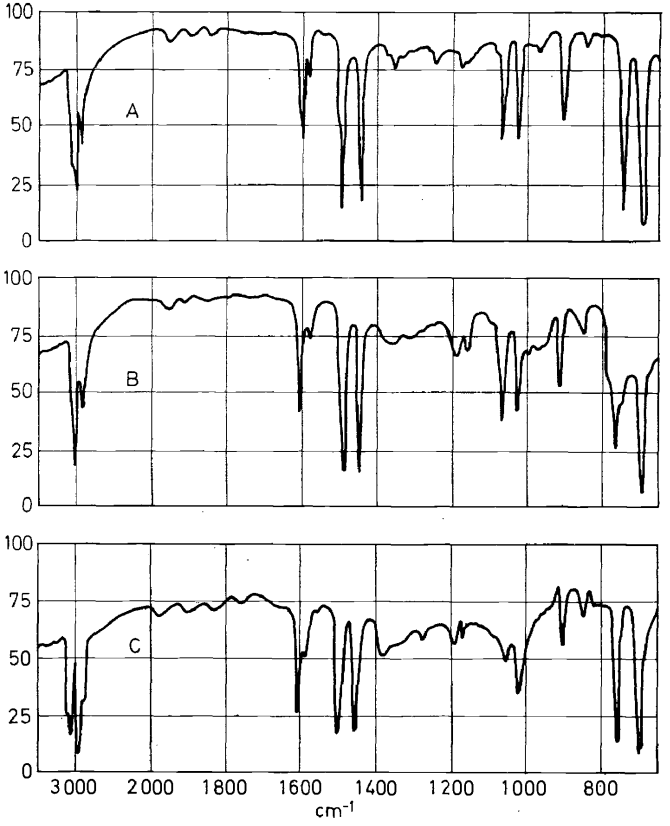


Figure 3. Infrared spectra: A, Polybenzylidene from benzaltosylhydrazone; B, Polybenzylidene from phenyldiazomethane with BF_3-catalyst at −60°C; C, Polystyrene from free radical polymerization

instead of methanol. With *t*-butanol or ethylene glycol the per cent of polymer decreases appreciably; this effect however, should not be attributed only to a difference in chemical structure, but also to differences in the composition of both aqueous and benzene phases.

Under similar reaction conditions several analogous tosylhydrazones were decomposed into polyarylidenes; the results are summarized in *Table 2.* Similarly copolymers can be easily obtained from tosylhydrazone mixtures. Contrary to expectations, polymerization did not occur from tosylhydrazones of acetone, acetophenone, benzophenone, *p*-dimethylamino-, *p*-acetamino- and *p*-nitro-benzaldehydes, furfural and 4-pyridine-aldehyde.

The formation of polyarylidenes by thermal decomposition of aryldiazoalkanes can also be carried out in homogeneous solution, e.g. mixtures of an aprotic solvent (benzene, toluene, diethylether) with an alcohol (methanol, isopropanol), or in pure methanol; in this last case however the polymer precipitates progressively.

It was found that the presence of alcohol is indispensable for polymer production; in the presence of diethylether or thioether, tetrahydrofuran,

acetonitrile, aniline, di- and triethylamine instead of alcohol, no polymerization occurs; only with ethyl mercaptan 6 per cent polymer has been isolated. In the absence of alcohol, phenyldiazomethane decomposes at 70°C in benzene solution (0·2 and 1 mole $l.^{-1}$) in the presence of radical initiators, as benzoyl or lauroyl peroxide, azo-bis-isobutyronitrile (0·2 to

Table 2. Polyarylidenes $\left[\begin{array}{c}-CH-\\ |\\ Ar\end{array}\right]_x$ from tosylhydrazones in water–methanol–benzene (4:1:5) in alkaline medium

Ar	*Yield* (%)	$\overline{M}_n$	*x*
C_6H_5	85	5·900†	65
p-Br.C_6H_4	72	6·000	35
p-Cl.C_6H_4	70	6·500	52
O-MeOC_6H_4	92	1·200	10
m-MeO.C_6H_4	70	5·900	50
p-MeO.C_6H_4	71	720	6
α-naphthylidene	22	1·500	10
β-naphthylidene	45	4·800	34
	72‡	10·000	71
9-anthranylidene	89	800	4
m-pyridilidene	10	2·330	26
C_6H_5/*p*-BrC_6H_4 (1:1)	80	6·000	
C_6H_5/*m*-MeOC_6H_4 (1:1)	70	5·500	
C_6H_5/*p*-Cl.C_6H_4 (1:1)	80	11·000	

† On fractionation from benzene solution by methanol addition 1/3 of the polymer precipitates at a methanol volume fraction (γ-value) = 0·17. The molecular weight of this fraction is equal to $\overline{M}_n$ 15·600.

‡ Solvent volume ratio water–methanol–benzene 25:15:60.

2 mole × 10^{-2} $l.^{-1}$) with formation of azine and stilbene without any polymer. The same reaction products were found by thermal (85°C) decomposition in anhydrous acetonitrile, while in aqueous acetonitrile the rate increases with added water, and some benzyl alcohol is also found[32]. At high peroxide concentration [(phenyldiazomethane)/(Bz_2O_2) = 2] and at 80°C, Lind and Fahr[33] isolated benzaldehyde, some benzylidenedibenzoate $C_6H_5CH(OBz)_2$ and 1,2-diphenylethylene glycol dibenzoate (Ph—CHOBz—)$_2$.

On the other hand, the polymerization reaction proceeds as well when the benzene–methanol (9:1) solution is prepared by the high vacuum technique, as when refluxed in air; moreover the percent polymer decreases on addition of increasing concentration of benzoylperoxide. All these data not only stress the important rôle displayed by the alcohol, but show also that the polymerization reaction cannot be a true radical reaction.

The influence of the methanol concentration on the extent of the polymerization reaction has been examined, and the data are summarized in *Table 3.*

Table 3. Polymerization by decomposition of phenyldiazomethane in high vacuum: Influence of the methanol concentration on the yield of polymer and $\overline{M}_n$

(MeOH) (mole l.$^{-1}$)	0·04	0·1	0·2	0·4	0·7	0·9	1·2	2·5	3·4	4·9	12·4	24·8 (100%)
Azine (%)	11	10·1	9·3	9	6·6	6·4	0·6	0·6	0·6			
Polymer (%)	0·6	3·5	28·8	33	74	80	92	95	96	93	94	95
$\overline{M}_n$				2730		4100		4880			5030	5090

Reaction conditions
The reaction conditions used were as follows:

$(C_6H_5CHN_2)$ = 0·2 M
Temperature = 70°C
Solvent = benzine

At low alcohol concentration the total yield of polymer increases with the alcohol content, then it levels off and remains constant at 90–95 per cent conversion for 10 volume per cent alcohol. With respect to the structure of the alcohol, some data are reported in *Table 4* and show that the reaction proceeds with difficulty in the presence of a tertiary alcohol.

Table 4. Influence of the alcohol
[PhDZ] = 0·2; (ROH) = 2·5 mole l.$^{-1}$;
diluent = benzene; high vacuum technique; temp. = 70°C

Alcohol	*Time for decolorization* (min)	*Conversion polymer* (%)	$\overline{M}_n$
Methanol	15	94	4670
Isopropanol	20	84·5	5320
t-Butanol	60	9·5	2200

The kinetic study of this polymerization is difficult on account of the great difficulty in preparing pure aryldiazomethanes. The HgO-oxidation of the benzalhydrazone produces indeed phenyldiazomethane of which the degree of purity, as determined by benzoic acid titration, depends on the solvent used. Prepared in benzene it varies from 40 to 60 per cent; besides isolated azine and stilbene, it contains small amounts of some volatile mercury-derivative[35–37] (not isolated) that is believed to exert an inhibiting effect on the polymerization and is taken as responsible for the relative lack of reproducibility of the rate measurements. Prepared in pentane the degree of purity attains 80–85 per cent; further purification is unsuccessful even by high vacuum distillation, due to the unstability of the aryl diazoalkane and the high reactivity of the phenyl carbene. The kinetic measurements were therefore carried out with 80–85 per cent pure phenyl diazomethane; it was verified that the amount of polymer formed, as determined gravimetrically, corresponds to the decrease of phenyldiazomethane, as

titrated with benzoic acid. The order of reaction with respect to the initial phenyldiazomethane concentration varied from 2 in diluted systems to 0·45 in more concentrated ones, the rates being evaluated graphically from conversion/time curves after the inhibition period.

Table 5. Rate of polymerization of phenyldiazomethane (PhDz) in benzene–methanol solution.
[MeOH] = 2·5 mole $l.^{-1}$; temp. = 45°C

$[PhDz]_{init.}$ (mole $l.^{-1}$)	*Initial rate* × 10^3 (mole $l.^{-1}$ min^{-1})	*Inhibition period* (min)
0·152	7·8	39·5
0·102	9·1	68
0·077	5·6	71·5
0·045	3·9	82
0·023	1·0	145

The overall activation energy of polymerization could only be evaluated from measurements in a relatively narrow range of temperature and was found equal to 5·5 kcal/mole (*Table 6*). *Tables 5* and *6* show also that

Table 6. Activation energy of polymerization of phenyldiazomethane in benzene–methanol solution.
[PhDz] = 0·09 mole $l.^{-1}$; [MeOH] = 2·5 mole $l.^{-1}$

Temperature (°C)	*Initial rate* × 10^3 (mole $l.^{-1}$ min^{-1})	*Inhibition period* (min)
40	0·9	110
45	1·7 1·5	123 132
50	3·6	67
55	4·2	56

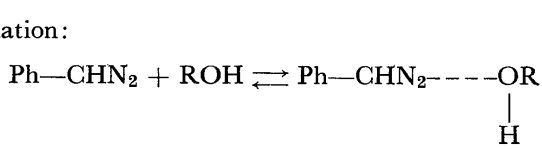
inhibition periods are not only temperature dependent but are also influenced by the monomer concentration.

On the basis of these results it is not possible to elucidate the reaction mechanism of this polymerization of phenyl diazomethane. The reaction is inhibited by oxygen, *m*-dinitrobenzene, benzoquinone and diphenylpicryl hydrazil; *p*-nitrophenyldiazomethane does not polymerize or copolymerize with phenyldiazomethane. These statements suggest rather a free radical mechanism.

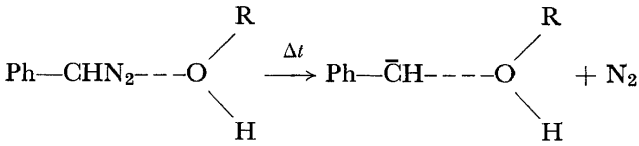
The absence of polymerization initiation with added peroxides, as mentioned previously, the failure of copolymerization of phenyldiazomethane with other vinyl monomers as *p*-chlorostyrene and methyl methacrylate (polybenzylidene being formed only) and the rôle of the alcohol are indicative for a more complex mechanism with formation of an aryldiazoalkane–methanol molecular complex. It must, however, be pointed out that the ultraviolet, infrared and visible spectra of phenyldiazomethane in cyclohexane remain unchanged on methanol addition, so that it was not possible

to take this complex in evidence. The following reaction mechanism could be written

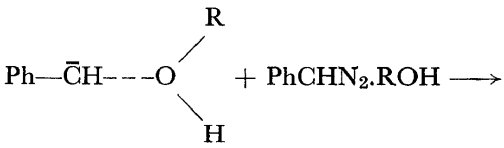
Complex formation:

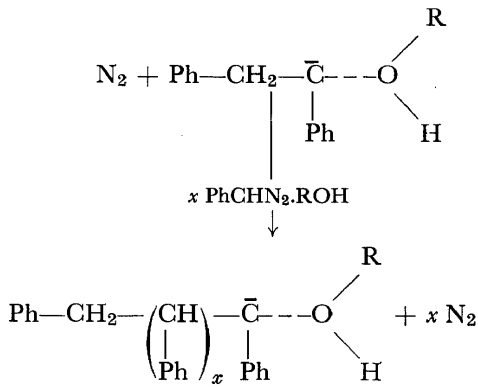


Initiation:

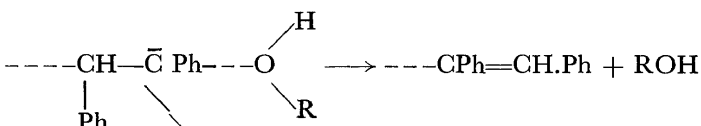


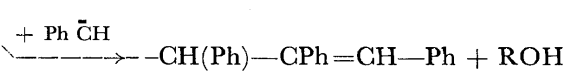
Propagation:





Termination:





The initiation step results from the thermal decomposition of the phenyl diazomethane–methanol complex. The reactivity of the phenylcarbene would be diminished by complexation with the methanol; it would propagate, either by insertion between the C—H bond of a next phenyldiazomethane molecule, or by addition followed by isomerization. It was also found that using CD_3OD instead of CH_3OH no deuterium was built into

the polymer (n.m.r. analysis); the methanol does not therefore participate in the hydrogen isomerization during the propagation steps. The termination reaction can proceed monomolecularly by internal rearrangement or bimolecularly through carbene dimerization.

This reaction mechanism, although not demonstrated, can account for the experimental results, and is essentially based on the low reactivity of diazoalkanes towards alcohol in the absence of any acid hydrogen.

Copolymerization experiments were also carried out in order to clarify the nature of the reaction mechanism. It is well known indeed that the copolymerization reactivity ratios differ considerably according to the free radical or ionic reaction mechanism by which the copolymers are obtained. Therefore copolymers were prepared at 70°C in benzene–methanol (4:1) solution starting from mixtures of two aryldiazoalkanes in different concentration ratios; other copolymers were also prepared following the heterogeneous method in water–methanol–benzene mixture (4:1:5) by decomposition in alkaline medium of the corresponding *N*-tosylhydrazone mixtures. In this last case the ratio of both diazoalkane components is uncertain on account of possibly different rates of decomposition of the corresponding tosylhydrazones and the presence of side products (azines).

The results are reported in *Tables 7* and *8*; DAz refers to the results obtained in homogeneous system directly from diazoalkanes, previously distilled and isolated, while THy correspond to the tosylhydrazone technique.

Table 7. Copolymerization of phenyl- (M_1) and *p*-chlorophenyl- (M_2) diazomethanes (Temp. = 70°C)

Molar ratio		*Time* (min)	*Yield* (%)	*Chlorine* (%)	f_1
1/3	THy	30	8·7	20·84	0·346
	DAz	40	2·8	19·03	0·407
1/1	THy	30	4·6	14·5	0·567
	DAz	80	3·6	12·6	0·636
3/1	THy	30	8·1	8·51	0·77
	DAz	80	2·8	7·47	0·796

THy: from tosylhydrazones; $r_1 = 0{\cdot}97$, $r_2 = 0{\cdot}50$.
DAz: from diazoalkanes; $r_1 = 1{\cdot}2 \pm 0{\cdot}1$, $r_2 = 0{\cdot}3 \pm 0{\cdot}05$.

The discrepancies between the r_1 and r_2 values result from the uncertainties relative to the concentration of the diazoalkanes in the tosylhydrazone technique. Nevertheless these values differ considerably from the r_1 and r_2 values of the corresponding styrene monomers, which are $r_1 = 0{\cdot}74$ and $r_2 = 1{\cdot}02$ for a free radical polymerization, and $r_1 = 2{\cdot}1$ and $r_2 = 0{\cdot}35$ for cationic polymerization[37, 38].

Similar results for the phenyl and *p*-bromophenyl derivatives are reported in *Table 8*.

Table 8. Copolymerization of benzylidene with *p*-bromobenzylidene

Molar ratio of tosylhydrazones	*Time* (min)	*Yield* (%)	*Bromine* (%)	f_1
1/3	60 75 120	0·77 32·8 57·7	33·88 37 36·4	0·368
1/1	50 75 120	5·3 39·5 32·9	27·62 29 28·33	0·569
3/1	20 24†	9·1 80·2	17·22 17·26	0·758

† Time in hours.

From these data, it results that $r_1 = 0{\cdot}85$ and $r_2 = 0{\cdot}40$. For the free radical polymerization of styrene and *p*-bromostyrene, the corresponding values are $r_1 = 0{\cdot}7$ and $r_2 = 1$ (ref. 39).

Consequently the results of these copolymerization experiments do not allow definite conclusions to be drawn with respect to the free radical or ionic mechanism of these diazoalkane–methanol polymerizations; they are indicative rather of a different process, and agree therefore with the reaction scheme as suggested for the homopolymerization itself.

Finally, one should mention some attempts made in order to copolymerize phenyldiazomethane with *p*-chlorostyrene. The content of *p*-chlorostyrene units is always low, e.g. 8 mole per cent for a 1:1 mixture; at higher chlorostyrene-phenyldiazomethane ratios (5:1 or 10:1) diphenylpyrazoline is formed through 1,3-dipolar addition of the diazo-group on the olefinic double bond; this pyrazoline is progressively transformed into 1-chlorophenyl-2-phenyl-cyclopropane. These side reactions render these experiments worthless for further elucidation of the reaction mechanism.

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