Translated from *Uspekhi Khimii*, 48, 344-361 (1979) U.D.C. 547.914

Trimerisation Polycondensation of Aromatic Acetyl Compounds and Their Ketals†

M.M.Teplyakov

The methods of synthesis, principal properties, and aspects of the application of polyphenylenes obtained by the trimerisation polycyclocondensation (PCC) of aromatic acetyl compounds or their ketals are examined. Attention is concentrated on the analysis of the influence of the conditions of synthesis on the cyclisation process.
The bibliography includes 51 references.

CONTENTS

I. Introduction 189
II. PCC of aromatic acetyl compounds 189
III. PCC of the ketals of aromatic acetyl compounds 190
IV. Practical applications of polyphenylenes based on aromatic acetyl compounds and their ketals 196

I. INTRODUCTION

One of the promising classes of thermostable polymers comprises polyphenylenes, the high thermal and chemical stability of which make it possible to use them as binders for various reinforced and antifriction materials and for other purposes.

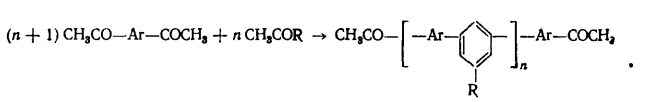
Polyphenylenes are synthesised nowadays in various ways using a wide variety of initial monomers[1,2]. The known methods for the formation of polyphenylenes suffer from various disadvantages. Progress in the field of synthesis and particularly in the application of polyphenylenes will be determined primarily by advances in the synthesis of polymers capable of being easily worked to form various articles, i.e. polymers which are readily soluble in organic solvents, and the methods of their synthesis should be technologically viable and based on available initial monomers.

The present review deals with the synthesis and properties of polyphenylenes obtained by the trimerisation polycyclocondensation (PCC) of acetyl compounds (methyl ketones) or their ketals. On the one hand, trimerisation PCC is genetically related to polycyclotrimerisation processes, which have been considered in detail in a review[3], and on the other, this process is a specific form of PCC, the general characteristics of which have already been examined[4]. In the present review attention is concentrated on factors influencing cyclisation, since, depending on the process conditions, both the degree of completion and specific features of PCC may vary and the contribution of the branching and cross-linking reactions may increase. This can ultimately lead to an increase of the fraction of defective structures which impair the useful properties of polymers (defective sections are as a rule least thermostable and are the first to undergo degradative processes).

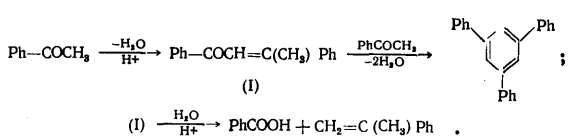
II. PCC OF AROMATIC ACETYL COMPOUNDS

The use of aromatic di- and mono-acetyl compounds as the initial monomers under PCC conditions made it possible to develop a new method for the synthesis of polymers of the polyphenylene type[5]. The method is based on the cyclocondensation of methyl ketones (acetone[6], acetophenone[7], and various aryl methyl or alkylaryl methyl ketones[8,9]) in the presence of acid catalysts, which has been known for a long time in organic chemistry.

Under the conditions of equal reactivities and without allowance for side reactions, polycyclocondensation involving the formation of polyphenylenes can be represented schematically as follows:



The actual process is complicated by side reactions, mainly incomplete cyclisation, and the unequal reactivities of the monomers. The cyclisation of aryl methyl ketones with formation of a benzene ring in an acid medium[8] proceeds via a dimer stage dypnone (β-methylchalcone), but dypnone can react with the liberated water to form an acid and α-methylstyrene[10]:

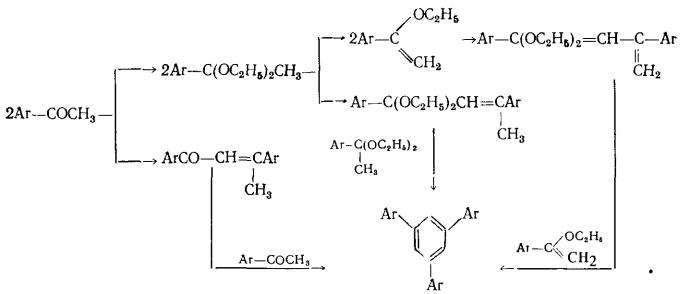


Acids or Lewis acids, which can simultaneously bind the water formed (H_2SO_4, $ZnCl_2$, polyphosphoric acid, BF_3, $BeCl_2$, $AlCl_3$, $AlBr_3$, dry HCl, and others) as well as certain other compounds, are therefore used as PCC catalysts[5]. The specificity of the formation of polyphenylenes under these conditions is open to doubt, since the yield of triphenylbenzenes from acetophenone does not exceed 20–50%.[9]

Korshak and coworkers[11,12] suggested that PCC of aromatic di- and mono-acetyl compounds be carried out in the presence of dry HCl and ethyl orthoformate in an inert solvent at approximately 20°C and put forward a

†Review commemorating the 70th Birthday of Academician V. V. Korshak.

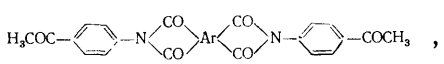
mechanism for the elementary step involving the formation of polyphenylenes under the conditions indicated:



The PCC reaction in solution was stopped at the stage of soluble polyphenylenes with a relatively low molecular weight and residual end groups (fore-polyphenylenes), which were isolated and then converted on heating above 250°C into three-dimensional polymers as a result of further condensation of the end groups. By carrying out the process in two stages, it was possible to convert the polymers into finished articles in the second stage. The monomers used were acetophenone, *p*-diacetylbenzene, di(acetylphenyl) ether, diacetylbiphenyl, and other compounds. Equimolar or nearly equimolar proportions of the initial monomers proved to be optimal[12]. A detailed chemical study of pre-polyphenylenes obtained by the above procedure[13] showed that the chain contained approximately two defective dypnone fragments.

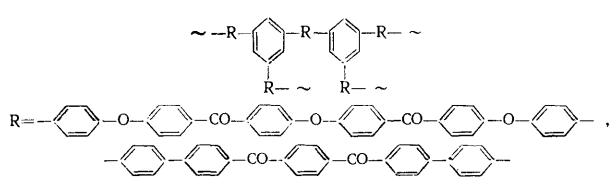
The employment of a single bifunctional monomer (diacetylferrocene) by Schlögl and Soukup[14] in an analogous process led to the formation of a three-dimensional product which could not be worked.

The use of bisacetylimides having the general formula



which made it possible to obtained cross-linked thermostable polymers by thermal polycyclocondensation, proved to be of interest[15]. The authors note that, when the process is carried out at 400°C without a catalyst, the product contains a fairly large number of defective structures, namely dypnone structures.

Zaitsev and coworkers[16,17] obtained cross-linked polymers having the general formula



and investigated their thermal stability.

Polymers based on the diacetyldibenzyl derivatives of *o*-, *m*-, or *p*-carbaboranes, obtained in the presence of HCl and ethyl orthoformate, proved to be the most thermostable[18,19]. The pre-polymers obtained with an average molecular weight of 1100–4600 contained, together with 1,3,5-triphenylbenzene units, also dypnone fragments and acetyl and ketal end groups. They were all readily soluble in many organic solvents: chloroform, toluene, dioxan, acetone, and others. After heat treatment at 400–450°C, they were converted into three-dimensional polymers with high thermal stability and heat resistance (according to the results of thermogravimetric analysis, no weight loss was observed on heating in air up to 900°C).

III. PCC OF THE KETALS OF AROMATIC ACETYL COMPOUNDS

Use of ketals of aromatic acetyl compounds makes it possible to carry out the PCC process more specifically and with formation of less defective structures. Korshak et al.[20] proposed a method for the synthesis of polyphenylenes from the ethyl ketals of aromatic di- and mono-acetyl compounds under conditions analogous to the PCC of aromatic acetyl compounds in the presence of ethyl orthoformate.

1. The Study of the PCC of Ketals in Model Reactions

The optimum conditions for the synthesis of polyphenylenes were discovered in the cyclocondensation of the acetophenone ketal[21,22], which simulates the PCC process. The efficiencies of various acid catalysts were estimated in this model reaction[21]. It was found that gaseous hydrogen chloride, the chlorides of inorganic and organic acids which form HCl on interaction with the alcohol liberated in the synthesis, and toluene-*p*-sulphonic acid are the most efficient catalysts. The high catalytic activity of HCl is associated with the ease of its dissociation in aprotic solvents: $HCl \rightleftharpoons H^+ + HCl_2^-$. It was established[22] that the maximum yield of 1,3,5-triphenylbenzene in the presence of HCl is observed at an initial ketal concentration in solution of approximately 1 M, the relation passing through an extremum. It can be accounted for by the complexity of the cyclocondensation process, i.e. by the occurrence, together with trimerisation PCC, of various condensation and cyclocondensation side reactions.

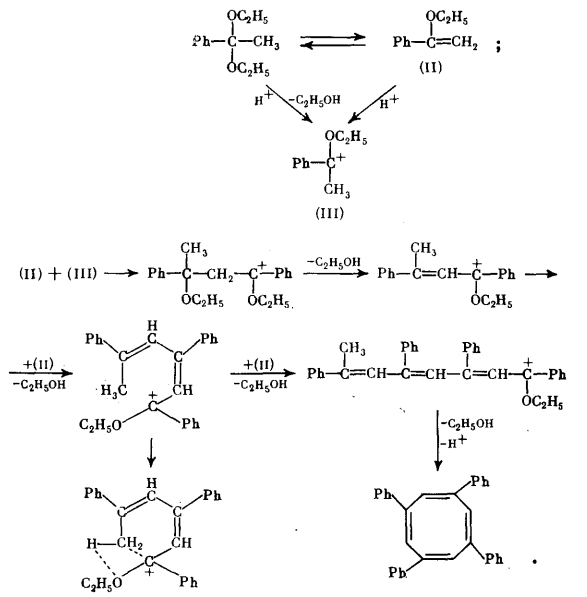
Table 1. The influence of solvent polarity μ on the yield of 1,3,5-triphenylbenzene (catalyst HCl, temperature 20°C, reaction time 1 h).

Solvent	μ	Yield %	Solvent	μ	Yield, %
Benzene	0.00	78	*m*-Cresol	1.54	43
CCl_4	0.00	72	Chlorobenzene	1.56	42
Toluene	0.29	76	Dimethylformamide	3.37	27
Dioxan	0.45	69	Nitrobenzene	3.99	29
$CHCl_3$	1.15	60			

The nature of the cyclocondensation of ketals is significantly influenced by the nature of the solvent (Table 1).[21] It was found that with increase of the polarity of the solvent, the yield of 1,3,5-triphenylbenzene falls. In highly polar solvents, such as nitrobenzene and dimethylformamide, the yield was less than 30%.

The study of the kinetics of the cyclocondensation of the acetophenone ketal under optimum conditions with respect to both the 1,3,5-triphenylbenzene formed[23] and the alcohol liberated in the course of cyclocondensation[21] showed that the process is of second order with respect to the ketal. The rate constants at 20°C, calculated by a second-order kinetic equation for various initial ketal concentrations, were approximately 1.2×10^{-1} litre mole^{-1} min^{-1}.

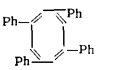
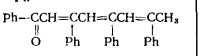
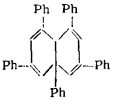
A mechanism for the cyclocondensation of ketals taking into account the kinetic data was proposed[21]. According to this mechanism, the cyclocondensation process proceeds as follows. Equilibrium is established in an acid medium with formation of α-ethoxystyrene from the acetophenone ketals. The addition of a proton to both the acetophenone ketal and to α-ethoxystyrene results in the formation of a carbonium ion. The subsequent interaction involves electrophilic attack by the carbonium ion on the carbon atom of the methylene group in α-ethoxystyrene, which is polarised owing to the presence of an oxygen atom next to the double bond of the vinyl ether group. Intramolecular elimination of the alcohol leads to the formation of a more stable form of the dimer, stabilised as a result of conjugation. Subsequent addition of yet another molecule to α-ethoxystyrene gives a trimer which is either converted into 1,3,5-triphenylbenzene via the formation of an intermediate complex followed by a cyclic electron transfer, or it interacts with a new α-ethoxystyrene molecule to form a tetramer, etc. The process can be represented schematically as follows:



The above scheme is confirmed by many facts, for example, the formation of triphenylbenzene in 68% yield from α-ethoxystyrene in benzene solution on treatment with HCl [21] and in addition by the mass-spectrometric analysis of the products of the cyclocondensation of acetophenone ketal[24]. Table 2 shows that, together with the main product (1,3,5-triphenylbenzene), the mixture contains α-ethoxystyrene, dypnone, 1,3,5,7-tetraphenylcyclo-octatetraene, a linear tetramer, and a cyclic pentamer, which, according to van Tamelen and Burkoth[25], should exist as 9,10-dihydronaphthalene. Analysis of the reaction mixture on a gas chromatograph combined with a mass spectrometer showed that the above compounds give rise to individual peaks corresponding to molecular ions. The presence of ketones is explained by the hydrolysis of the ketals in the course of isolation.

The proposed mechanism explains certain features of the cyclocondensation and polycyclocondensation of ketals. For example, the dependence of the yield of the trimer on the polarity of the medium, indicated above, can be accounted for by the effects of the stabilisation of the carbonium ion and the decrease of its reactivity.

Table 2. Mass-spectrometric analysis of the condensation products of the acetophenone ketal.

m/e	Compound corresponding to the molecular ion	Relative peak intensity, %		
		c_0^*=0.25 M	c_0=1.0 M	c_0=1.5 M
148	α-Ethoxystyrene	8	2.5	11.4
222	Dypnone	17	22	26
306	1,3,5-Triphenylbenzene	66	71	57.5
408		6.2	2.5	1.6
426		1.9	1.5	3.5
510		0.9	0.5	0

* Here c_0 is the initial ketal concentration.

As was to be expected from the Ruggli–Ziegler principle, as the initial acetophenone ketal concentration rises from 0.25 to 1.5 M, the content of macrorings diminishes and that of linear condensation products increases (Table 2).

The study of the temperature dependence of the yield of 1,3,5-triphenylbenzene showed that its maximum amount is formed at approximately 20°C.[21,23] An increase of temperature may prevent the formation of triphenylbenzene both due to the side reaction involving the addition of HCl to the vinyl ether group and in consequence of the decrease of the concentration of gaseous HCl in solution. The decrease of the yield at reduced temperatures can also be explained by factors other than the decrease of the reaction rate. It was found[23] that the kinetic curves for the formation of 1,3,5-triphenylbenzene below 20°C reach a limit and an increase of the duration of synthesis does not alter the yield of triphenylbenzene. The reduction of the temperature of the synthesis also leads to an increase of the inductive period. On the basis of these findings, the decrease of the yield is presumably associated with the difficulty of the formation at reduced temperatures of α-ethoxystyrene, which is formed spontaneously from the ketal at elevated temperatures. The fact that the yield of 1,3,5-triphenylbenzene is independent of whether the reaction is carried out in benzene solution presaturated with HCl or whether HCl is passed through the reaction mass during synthesis is of interest from the technological point of view[23].

In order to investigate the influence of the structure of the initial ketal on the cyclocondensation process, the ethyl ketals of 4-acetylbiphenyl, 4-acetylphenyl phenyl

ether, and 4′-acetyl-1,3,5-triphenylbenzene, as well as the butyl ketal of acetophenone were used[26,27]. At 20°C and with HCl passed through the system the reaction terminates after 25–30 min in all cases and its yield is fairly high (approximately 70%).[27] This may support the view that an increase of the number of benzene rings does not reduce the reactivity of the ketal. It is noteworthy that an increase of the number of benzene rings in the molecules of 1,3,5-trisubstituted oligophenyls reduces sharply their solubility. The introduction of a pivotal oxygen atom between the benzene rings greatly increases the solubility. The replacement of ethyl ketals by other alkyl ketals apparently has little effect on the nature of the cyclocondensation reaction[26].

The condensation of the acetophenone ketal in the range 100–400°C has also been studied[21,23]. Investigation by thin-layer chromatography of the condensation products obtained at 200°C in the presence of various catalysts showed that 1,3,5-triphenylbenzene is formed in the presence of acid catalysts. In the presence of alkaline catalysts and in the absence of a catalyst the condensation products contain only dypnone, α-ethoxystyrene, and the ketal which failed to react. The content of 1,3,5-triphenylbenzene in the reaction mass was estimated quantitatively by gas–liquid chromatography. The efficiency of the catalysts decreases in the sequence $TsOH.H_2O > H_2SO_4 > ZnCl_2 > SnCl_4$. An increase of the temperature of the synthesis leads to a decrease of the content of 1,3,5-triphenylbenzene in the reaction mass, while the overall yield of the condensation products is in all cases constant, i.e. the decrease of the yield of 1,3,5-triphenylbenzene is associated with the enhancement of the role of reactions leading to the formation of polyvinylenes[21].

Summarising the data for the cyclocondensation of the ketals of aryl methyl ketones, one may assume that the optimal conditions for the PCC of ketals obtain when the reaction catalysed by HCl is carried out in non-polar aromatic hydrocarbons at an initial concentration of the ketal groups of approximately 1*N* and at a temperature of 15–25°C or when the process is carried out at a higher temperature in the presence of $TsOH.H_2O$.

2. Characteristic Features of the PCC of Ketals

Taking into account the main features found with the aid of the model reaction, including the property of the PCC involving the possibility of a significant decrease of the solubility of polyphenylenes with increase of their molecular weight and gel formation, the synthesis of polyphenylenes was carried out in two stages[20]. Initially polyphenylenes with a relatively low molecular weight and residual reactive ketal or acetyl end groups were obtained in solution under the conditions of PCC; these forepolyphenylenes were then converted, on heating under processing conditions (conversion into finished articles), into the final polymers with a cross-linked structure.

The use of the ethyl ketal of *p*-diacetylbenzene as the initial monomer in the reaction carried out in benzene in the presence of HCl as the catalyst leads to the formation of a cross-linked polymer in a quantitative yield[28]. In the first step of the interaction the branching of the polymer already begins and subsequently leads to the rapid formation of a network structure. It is quite understandable that the process should depend on the amount of HCl. It was found that, with increase of the rate of supply of HCl, the duration of synthesis before the attainment of the gel formation point diminishes; the overall consumption of the catalyst remains constant for the given charge in the reactor. This type of relation is associated with the rate of saturation of the solution by hydrogen chloride, which, up to a certain value, is directly proportional to the rate at which hydrogen chloride is passed. It was found[23] that an increase of the rate of supply of HCl within certain limits entails a directly proportional decrease of the time of attainment of the gel formation point. With increase of the charge severalfold, it is necessary to increase by the same factor either the duration of synthesis or the rate of supply of the catalyst. Thus the synthesis of the polymer may be regulated by controlling the amount of catalyst.

In order to obtain polymers with higher molecular weights in the first stage and to suppress the branching reaction, joint PCC of the ketals of mono- and di-acetyl compounds was carried out[28]. Fig. 1, which presents the dependence of the gel formation time and the amount of the gel fraction in the joint PCC of the acetophenone and *p*-diacetylbenzene ketals on their initial molar ratio, shows that, with increase of the fraction of the monofunctional monomer, the rate of gel formation falls and the proportion of the soluble fraction increases. For a molar ratio of 1 : 2, gel formation is not observed in the course of 2.5 h, but an increase of the amount of blocking agent leads to a decrease of the molecular weight of the polymer and of the amount of terminal functional groups, which is undesirable for the subsequent hardening stage. All the polyphenylenes synthesised in this way were therefore obtained mainly with an equimolar ratio of the mono- and bi-functional monomers.

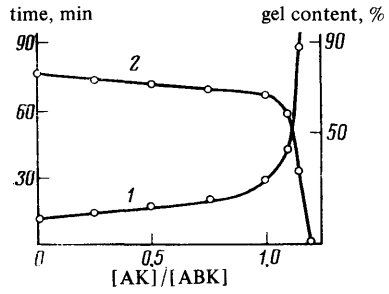


Figure 1. Dependence of the gel formation time (curve *1*) and of the amount of gel (curve *2*) in the PCC of the acetophenone ketal (AK) and the *p*-diacetylbenzene ketal (ABK) on their initial molar ratio.

In order to elucidate the nature of the PCC process, a thermodynamic study was made of the synthesis of polyphenylene from the ketals of acetophenone and *p*-diacetylbenzene[29,30]. The enthalpy of the process and the enthalpies of combustion and heat capacities of the monomers and polymers were determined. The enthalpies, entropies, and Gibbs free energies of formation of polyphenylene by PCC in solution and of its conversion into a three-dimensional polymer on heating were calculated from the results. Both processes are thermodynamically

allowed and their equilibria are almost completely displaced towards the formation of the corresponding polymer. Thus at 298.15 K the equilibrium constants K_e for the two reactions are respectively 1.5×10^{24} and 1.35×10^5. Thus the PCC of ketals in solution is known to be a non-equilibrium process, since, according to Korshak's definition[31], non-equilibrium processes are those for which $K_e > 10^3$.

The chain conjugation energy in the three-dimensional polyphenylene has been estimated[31]. Having assumed to a first approximation that the energy of the van der Waals interaction in this polymer is close to the analogous value in crystalline *m*-terphenyl, it was found that the chain conjugation energy is 62.5 kJ mole^{-1}, which agrees with the estimated chain conjugation energy in the polyphenylene obtained by the polycyclotrimerisation of phenylacetylene with *p*-diethynylbenzene[32].

Table 3. Kinetics of the PCC of the ethyl ketal of *p*-diacetylbenzene (20 °C, initial concentration 0.5 M, HCl concentration 0.2 M).

Time, min	Current ketal concn., M	k_1, litre mole^{-1} min^{-1}	k_2, litre mole^{-1} min^{-1}
0.35	0.225	1.96	—
0.5	0.201	1.90	—
0.65	0.177	2.02	—
0.75	0.164	2.03	—
1.0	0.151	2.03	—
2.0	0.127	—	0.172
3.0	0.119	—	0.177
4.0	0.115	—	0.198
5.0	0.113	—	0.162
7.0	0.104	—	0.171
10.0	0.096	—	0.192
		k_{av} = 1.99	k_{av} = 0.18

Taking into account the non-equilibrium nature of the PCC of ketals, the reaction kinetics were studied in benzene solution in the presence of dry HCl,[23,33-35] the aim being to elucidate the sequence of the interactions of the above monomers, to be able to achieve their optimal selection for the synthesis of polyphenylenes, and to elucidate the dependence of the reactivity of the monomers on their structure. The kinetics of the cyclocondensation and polycyclocondensation of the acetophenone, 4'-ethylacetophenone, 2-acetylfluorene, 4'-acetyl-1,3,5-triphenylbenzene, *p*- and *m*-diacetylbenzene, 4,4'-diacetylbiphenyl, and di-(4-acetylphenyl)methane ketals were studied. The cyclocondensation of the monoketals is a second-order reaction and its rate constants are close to the rate constant for the cyclocondensation of the acetophenone ketal, i.e. the rate of reaction is almost independent of the structure of the chosen monoketals. In contrast to this, the kinetics of the PCC of diketals, for example, the diketal of *p*-diacetylbenzene, involve two sharply differentiated regions (Table 3).[23] The rate constant in the second kinetic region shows no tendency to decrease and is an order of magnitude lower than in the first region. Data for other diketals are presented in Table 4.[33] They were calculated in addition by the method of Frost and Schwemer for parallel-consecutive reactions. The different reactivities of the functional groups (cf. No. 1 and No. 4 in Table 4) are associated with the activation of the carbonium ion formed from the first ketal group owing to the electron-accepting properties of the second group transmitted via the conjugation system of the benzene ring. Naturally the introduction of groups which interrupt the conjugation system or the absence of an *M*-effect in the *m*-position of the benzene ring lead to a value of k close to those of the rate constants for monofunctional compounds. Thus the properties of the initial ketal can influence the structure and properties of the polyphenylenes produced by the reaction. It has been shown[36] that, when the ketal of *m*-diacetylbenzene is used, the formation of high-molecular-weight polyphenylenes in PCC in solution is hindered by the formation of *m*-phenylene macrocyclic structures, the smallest of which should be a substituted cyclohexa-*m*-phenylene fragment. This nature of the process also explains the appreciable decrease of k_2 compared with k_1 in the PCC of the *m*-diacetylbenzene ketal (Table 4).

Table 4. The rate constants for the PCC of the ketals of aromatic acetyl compounds*.

No.	Initial compound	k_1, litre mole^{-1} min^{-1}	k_2, litre mole^{-1} min^{-1}	k'_1, litre mole^{-1}min^{-1}	k'_2, litre mole^{-1} min^{-1}
1	Ethyl ketal of *p*-diacetylbenzene	1.99	0.18	2.34	0.49
2	Ethyl ketal of *m*-diacetylbenzene	0.165	0.01	0.22	0.028
3	Ethyl ketal of di-(4-acetylphenyl)methane	0.16	—	0.175	—
4	Ethyl ketal of 4,4'-diacetylbiphenyl	1.2	0.5—0.7	1.73	**

*Rate constants calculated by the method of Frost and Schwemer are designated by k'_1 and k'_2.
**The value of k_2 for the polycyclocondensation reaction is approximately an order of magnitude lower than k_1.

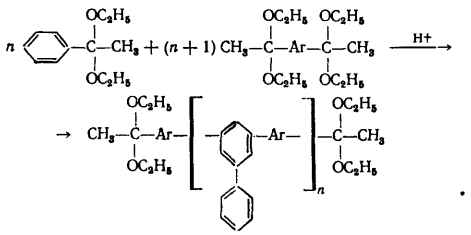
A study by infrared spectroscopy of the hardening of polyphenylenes at 350 °C in the presence of a catalyst showed[37] that it results in an increase of the number of 1,3,5-trisubstituted benzene rings, i.e. further trimerisation PCC of the end groups of the polyphenylene takes place.

The PCC of di- and mono-ketals can be carried out in such a way that polyphenylenes without reactive end groups are formed. For this purpose, one uses an excess of the mono-ketal, whose introduction leads simultaneously to chain termination. Thus when the *p*-diacetylbenzene ketal and a sixfold excess of the acetophenone ketal were used, an oligomer consisting mainly of a branched oligophenyl with 13 benzene rings was obtained. Judging from gel permeation chromatographic data (Fig. 2), the oligophenyl is identical with the model compound synthesised by the trimerisation cyclocondensation of the ketal of 4'-acetyl-1,3,5-triphenylbenzene[50].

3. The Synthesis of Polyphenylenes from Ketals Having Various Structures and Their Properties

If it is assumed that the reactivities of the ketals of mono- and di-acetyl compounds in PCC are close and in addition that there are no side reactions, the hypothetical linear polyphenylene (pre-polymer) should be obtained

for an equimolar component ratio. The syntheses were therefore carried out using equimolar ratios of the initial ketals. In this case the reaction can be represented schematically as follows:



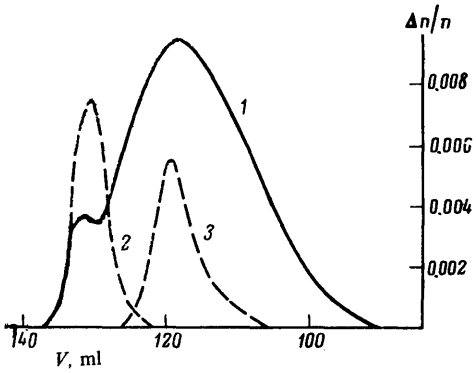
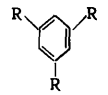


Figure 2. Gel permeation chromatography of the products of the PCC of the ketals of *p*-diacetylbenzene and acetophenone in molar proportions of 1 : 6 (curve *1*), 1,3,5-triphenyl benzene (curve *2*), and the oligophenyl



(curve *3*), where

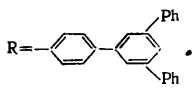
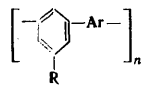


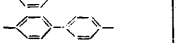
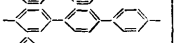
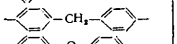
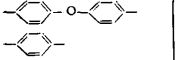
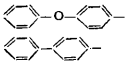
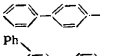
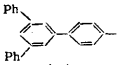
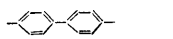
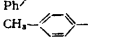
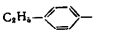
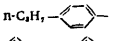
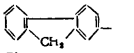
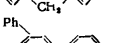
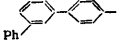
Table 5 presents certain properties of polymers based on the ketals of diacetylarylenes and acetophenone. The pre-polymers synthesised consisted of slightly coloured powders, readily soluble in ordinary organic solvents. The formation of a 1,3,5-trisubstituted benzene ring and the occurrence of the joint polycyclocondensation of the ketals of diacetylarylenes and acetophenone were confirmed by infrared spectroscopic data[37,40]. An increase in the content of *para*-substituted benzene rings in the main chain of the pre-polymer leads to a sharp decrease of the solubility of the polymer, while in the case of the ketal of 4,4″-diacetyl-*p*-terphenyl the pre-polymer is soluble only in nitrobenzene. The introduction of bridge groups such as –O– and $-CH_2-$ increases the mobility of the individual units of the molecule and reduces the softening temperature (Table 5), which is very important for the processing of the polymer. However, the introduction of the above connecting groups reduces the thermal stability of the final three-dimensional polymers obtained by the heat treatment of the fore-polymers.

The modification of the pre-polymers by altering the structure of the monofunctional monomer is of interest from this point of view[38,39] (Table 5). The pre-polymers synthesised in this way from the *p*-diacetylbenzene ketal are readily soluble. The highest solubility was observed in dichloroethane, dioxan, and chloroform. Comparison of the solubilities in toluene (Table 5) showed that the polymer with the most bulky side group, such as that derived from 1,3,5-triphenylbenzene, has the highest solubility.

Table 5. The properties of pre-polyphenylenes having the general formula

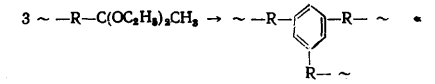


and based on the ketals of diacetylarylenes and monoacetyls.

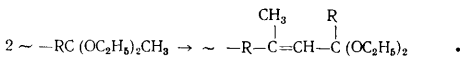
Structure of initial monomers		η_{int} in $CHCl_3$, dl g^{-1}	Solubility			Refs.
–Ar	R		in toluene (quantitative solubility, g $litre^{-1}$)	in $CHCl_3$	in nitrobenzene	
	Ph–	0.08	+ (14)	+	+	20, 28
	Ph–	0.07	–	+	+	20, 28
	Ph–	0.07*	–	–	+	22
	Ph–	0.14	+ (>200)	+	+	36
	Ph–	0.12	+	+	+	20, 28
	Ph–	0.08	+ (>200)	+	+	20, 28
		0.06	+ (30)	+	+	38
»		0.04	+ (33)	+	+	38
»		0.08	+ (50)	+	+	39
		0.14	+ (10)	+	+	39
»		0.25	+ (>200)	+	+	39
»		0.14	+ (>200)	+	+	39
»		0.11	± (2)	+	+	39
»		0.12	+ (10)	+	+	39
		0.09	+ (50)	+	+	35

*The measurements were made in nitrobenzene.

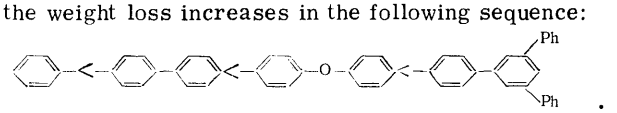
The pre-polymers synthesised were heat-treated in order to convert them into the final three-dimensional polymers with high thermal stability and heat resistance[20, 22,23,35]. The polymer may be cross-linked in two ways. Firstly, by the interaction of three end groups it is possible to form a new 1,3,5-trisubstituted benzene ring via the mechanism



Secondly, when two end groups interact, condensation may take place with formation of dypnone fragments and then polyvinylenes:



The second type of interaction leads to the appearance of defective fragments in the polymer structure. It was shown that the highest thermal stability and heat resistance are exhibited by fully aromatic polymers[23,28] or polymers with an aromatic main chain[38,39]. Thus a hardened polymer with the oxygen bridge group in the side chain begins to decompose at a temperature approximately 70°C higher than a polymer with the same group in the main chain. The study of the thermal degradation in an inert atmosphere of the polyphenylenes based on the *p*-diacetylbenzene ketal with various side groups showed that the weight loss increases in the following sequence:



This is apparently associated with the elimination of phenyl side groups.

Together with thermogravimetric analysis, the method involving pyrolysis in a closed volume with subsequent gas-chromatographic analysis of the volatile degradation product was used[23]. In order to discover to what extent the structure of the hardened products resembles that of polyphenylene, a study was made of the thermal stabilities of a number of model compounds containing 1,3,5-trisubstituted benzene rings[27]. The thermal degradation of the model compounds entails the liberation of hydrogen and methane alone, which are the main products of the decomposition of the benzene rings. The hardening of the prepolymers at 450°C gives rise to products in the pyrolysis of which hydrogen and methane are evolved in the same temperature range (>450°C) as for the model compounds. In the pyrolysis of the polymers hardened at 300°C hydrogen and methane appear at lower temperatures compared with the model compounds, which can be explained by the presence of end groups and defective fragments in the structure (Fig. 3).

Polymers based on the ketals of *p*-diacetylbenzene, 4,4′-diacetylbiphenyl, and 4,4″-diacetyl-*p*-terphenyl, hardened under optimal conditions, exhibit the highest thermal stability and heat resistance[23]. However, a disadvantage of these polyphenylenes is their low solubilities in the pre-polymer stage, which seriously limits their practical synthesis and in addition hinders polycyclocondensation to high degrees of conversion. The solution of the second problem, i.e. the synthesis of high-molecular-weight soluble polyphenylenes by one-stage PCC in solution, is undoubtedly a very attractive proposition, despite its entire potential complexity owing to the possibility of the formation of a network structure, since it would make it possible to extend the assortment of systems capable of practical utilisation. Several studies have been devoted to the solution of this problem[35,39,41].

The PCC of the *m*-diacetylbenzene ketal has been investigated[36,41] and polyphenylenes based on it have been synthesised. The choice of this monomer is dictated by the fact that, in view of the angular disposition of the benzene rings, *m*-polyphenylenes have a looser packing compared with *p*-polyphenylenes, which improves their solubility and lowers their melting point. However, the synthesis of high-molecular-weight polyphenylenes was hindered by the formation of macrocyclic *m*-phenylene fragments. The molecular weight (MW) characteristics and the molecular weight distribution (MWD) of the above polyphenylene have been studied[41]. Fractionation of the polymer led to the isolation of five fractions with $\overline{M}_w$ from 1400 to 115 000 and $\overline{M}_n$ from 1100 to 80 500. The MWD curves were plotted for each fraction in terms of the Shulz equation on the basis of the measured $\overline{M}_w$ and $\overline{M}_n$ for the fractions. The fore-polymer investigated has a fairly broad MWD and a coefficient of polydispersity of 7.6 (the coefficient calculated from the MWD curve is 7.3).

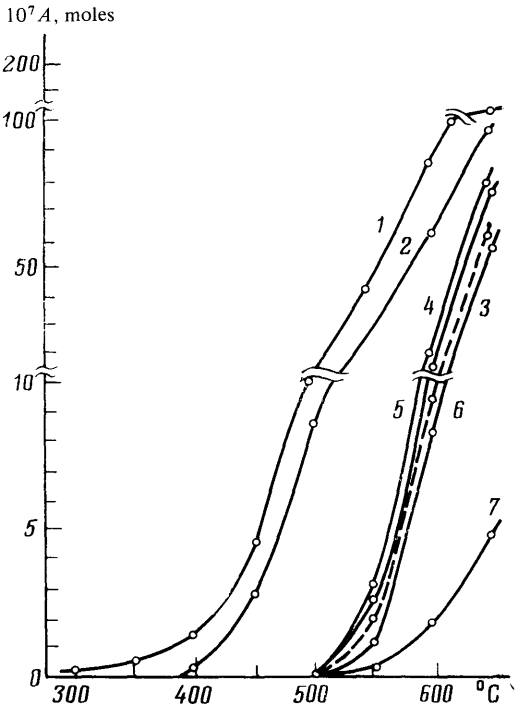
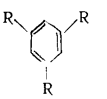
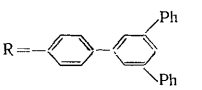


Figure 3. Methane evolution curves in the pyrolysis in a closed volume of the polyphenylene based on the *p*-diacetylbenzene and acetophenone ketals: 1) fore-polyphenylene; 2) fore-polyphenylene heat-treated at 300°C; 3) fore-polyphenylene heat-treated at 450°C; 4) the oligophenyl



where



5) 1,3,5-triphenylbenzene; 6) *m*-terphenyl.

Combined with a low intrinsic viscosity, this indicates a branched structure of the macromolecules. The coefficients of the Mark–Kuhn–Houwink equation for the first and second sections of the $\lg[\eta] - \lg\overline{M}$ relation were calculated and these too indicate a branched structure of

the polymers: $[\eta]_1 = 3.16 \times 10^{-4} \overline{M}_w^{0.6}$; $[\eta]_2 = 9.55 \times 10^{-4} \overline{M}_w^{0.22}$. For all the fractions, the increments in the refractive index and the specific partial volumes are similar. In other words, the degree of branching is similar for all the fractions. It is noteworthy that, for a comparatively low molecular weight of the initial pre-polymer, fractionation led to the isolation of a fraction with a fairly high molecular weight ($\overline{M}_w = 115\,000$). Unfortunately the proportion of this fraction proved to be very low, amounting to 2.5%.

The properties of polyphenylenes based on the ketal of 4,4′-diacetylbiphenyl, the most interesting monomer from the standpoint of its technological availability, and the thermal properties of the resulting polyphenylenes have been modified by synthesising copolymers with the *m*-diacetylbenzene ketal[36,39] and by introducing side groups into the polymer chain by altering the nature of the monofunctional monomer[38,39]. The introduction of *m*-phenylene fragments into the polymer chain was achieved by the joint PCC of the ethyl ketals of 4,4′-diacetylbiphenyl, *m*-diacetylbenzene, and acetophenone. The fore-polyphenylenes obtained were readily soluble in organic solvents, particularly when the initial mixture contained more than 75 mole % of the *m*-diacetylbenzene ketal. When mono-ketals having different structures were used (Table 5), it was found that the introduction of bulky substituents, for example, fluorene, triphenylbenzene, and diphenyl ether groups, causes only a slight alteration of the molecular weights and solubilities of polyphenylenes. In contrast to this, the introduction of alkyl substituents into the polymer side chain increases significantly the solubility and makes it possible to obtain polymers with a high molecular weight. For example, the PCC of the 4,4′-diacetylbiphenyl and *p*-ethylacetophenone ketals yields a fore-polymer with a viscosity of 0.25–0.30 dl g^{-1} and its $\overline{M}_w$ reaches 40 000–60 000; according to ^{1}H NMR data, the polyphenylene structure predominates in the polymer. This polymer is highly soluble in benzene and toluene in the cold (>200 g $litre^{-1}$).

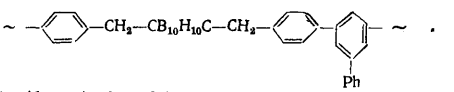
Table 6. The molecular weight characteristics of the fore-polymer based on the 4,4′-diacetylbiphenyl and *p*-ethylacetophenone ketals.

No. of fraction	Content, wt.%	$[\eta]$, dl g^{-1}	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	25.0	0.023	1 300	420	3.10
2	22.4	0.080	4 600	1 600	2.77
3	11.5	0.102	8 700	4 600	1.90
4	15.6	0.130	33 000	11 400	2.92
5	14.3	0.170	143 000	50 000	2.86
6	7.3	0.176	164 000	77 000	2.12
7	2.2	0.194	200 000	100 000	2.00
Initial fore-polymer	100.0	0.120	50 000	7 400	6.80

Polymers with ethyl side groups in the chain, pressed out at a high temperature, are hardly deformed up to the decomposition temperature (500 °C). In order to account for the causes of their very high thermal stability and heat resistance, a pre-polymer with blocked end groups was synthesised and its heat treatment yielded a highly thermostable product with a three-dimensional structure[39]. Consequently the ethyl group participates in the cross-linking process, which confirms the infrared spectroscopic data.

Thus the joint polycyclocondensation of *para*-substituted diketals with the *p*-ethylacetophenone ketal makes it possible to obtain polyphenylenes with a high solubility, a fairly high average molecular weight, and capable of being worked to form final articles with a high thermal stability. The study of the MWD of the pre-polyphenylene based on the ketal of 4,4′-diacetylbiphenyl and *p*-ethylacetophenone[35] demonstrated a fairly high polydispersity coefficient (6.8–9.9). The molecular weights of the polymer fractions isolated are listed in Table 6, which shows that, out of seven fractions, three have high molecular weights ($\overline{M}_w = 143\,000$–$200\,000$), their overall proportion being 25%. The MWD within the fractions were calculated from the Schulz equation and their summation yielded the overall distribution curve for the non-fractionated polymer. The MWD curve proved to be fairly broad, which confirms the branched structure of the polyphenylene investigated. Thus the possibility, in principle, of synthesising high-molecular-weight polyphenylenes with a non-cross-linked structure by the polycyclocondensation of ketals was demonstrated.

Polymers obtained by the PCC of carbaborane-containing ketals have been described recently[18,19,42]. Using the ethyl ketals of di-(4-acetylbenzyl)-*m*-carbaborane and acetophenone, a polymer with the following tentative structure of the elementrary unit was obtained:



However, in the study of the polymer it was noted that the contribution of the trimerisation polycyclocondensation to the overall polycondensation process was much smaller than in previous cases. The polymer was highly soluble in organic solvents at the fore-polymer stage and exhibited a high thermal stability in the final stage, showing no weight loss on heating in air to 900 °C according to thermogravimetric analysis.

IV. PRACTICAL APPLICATIONS OF POLYPHENYLENES BASED ON AROMATIC ACETYL COMPOUNDS AND THEIR KETALS

Polymers based on aromatic acetyl compounds obtained by the method of Korshak et al.[5] are used to make fancy articles and filled plastics exhibiting a high thermal stability and heat resistance as well as resistance to corrosive media[5,43]. They are of interest as binders for the formation of antifriction polymeric materials[45]. The decrease of the coefficient of friction of the composition based on a carbon fabric takes place in parallel with the decrease of the rigidity of the polymer chain. Polymers based on ketals, obtained by the method of Korshak et al.[20], are also of interest for the formation of a wide variety of thermostable and heat resistant materials, particularly glass and carbon plastics[23,44]. The modification of these polymers by the introduction of sulphide bridges into the chain yielded materials with an enhanced mechanical strength without decrease of thermal stability[46,47].

The presence of organoelemental fragments in the chains of polyphenylenes imparts specific properties to the latter. Thus polymers based on di-(acetylbenzyl)-carbaboranes and their ketals[18,19] exhibit an exceptionally high thermal

stability. Glass plastics with a working temperature of 400°C have been made from them. The use of cobaltocenium-containing diacetyls and acetophenones made it possible to obtain thermostable anion-exchange resins[48].

A disadvantage of polyphenylenes based on aromatic acetyl compounds and their ketals from the standpoint of their practical application is the high temperature of their conversion into the final three-dimensional polymers. This problem is solved by replacing the acetyl groups in the fore-polymers, obtained by the trimerisation of PCC, by more reactive groups, for example furfurylidene, hydroperoxy-, or nitrile groups[35], as well as cyanomethyl cinnamate[49] and dicyanopropylidene[51] groups.

---o0o---

Thus the use of the trimerisation PCC of aromatic acetyl compounds and their ketals not only expands our ideas about this process and about the dependence of the properties of polymers on their structure, but also makes it possible to obtain polymeric materials which are extremely valuable in practice.

REFERENCES

1. G. K. Noren and J. K. Stille, J. Polymer Sci., D-5, 385 (1971).
2. J. G. Speight, P. Kovacic, and F. W. Koch, J. Macromol. Sci., C5, 295 (1971).
3. V. A. Sergeev, V. K. Shitikov, and V. A. Pankratov, Uspekhi Khim. (in the Press).
4. M. M. Teplyakov and A. L. Rusanov, "Politsiklokondensatsiya, Entsiklopediya Polimerov" (Polycyclocondensation. The Encyclopaedia of Polymers), Izd. Sov. Entsiklopediya, Moscow, 1977, Vol. III, p. 86.
5. V. V. Korshak, M. M. Teplyakov, and V. V. Sergeev, USSR P. 302 022 (1971); Byul. Izobret., No. 36, 211 (1971).
6. R. Kane, J. prakt. Chem., 15, 129 (1838).
7. C. Engler and H. E. Bertold, Ber., 7, 1123 (1874).
8. R. E. Lyle, E. J. DeWitt, N. M. Nichols, and W. Cleland, J. Amer. Chem. Soc., 75, 5959 (1953).
9. H. O. Wirth, W. Kern, and E. Schmitz, Makromol. Chem., 68, 69 (1963).
10. R. C. Elderfield and J. P. King, J. Amer. Chem. Soc., 76, 5437 (1954).
11. V. V. Korshak, M. M. Teplyakov, and V. A. Sergeev, Vysokomol. Soed., B14, 800 (1972).
12. V. V. Korshak, M. M. Teplyakov, and V. A. Sergeev, Dokl. Akad. Nauk SSSR, 208, 1360 (1973).
13. V. A. Sergeev, V. K. Shitikov, L. G. Grigor'eva, R. A. Dvorikova, V. V. Korshak, and M. M. Teplyakov, Vysokomol. Soed., A20, 365 (1978).
14. K. Schlögl and H. Soukup, Monatsh., 99, 927 (1968).
15. E. A. Babenkova, T. S. Tsygankova, B. A. Zaitsev, V. S. Matrosov, and G. A. Shtraikhman, Vysokomol. Soed., B10, 746 (1976).
16. B. A. Zaitzev, Y. N. Sazanov, L. A. Shibaev, L. L. Dantsig, and T. A. Antonova, Termochim. Acta, 19, 319 (1977).
17. B. A. Zaitsev, G. I. Khramova, and G. A. Shtraikhman, USSR P. 517 577 (1975); Byul. Izobret., No. 22 (1976).
18. V. V. Korshak, M. M. Teplyakov, I. L. Gelashvili, L. I. Zakharkin, and V. N. Kalinin, "Tezisy Dokladov Respublikanskoi Konferentsii po Primeneniyu Polimernykh Materialov v Narodnom Khozyaistve" (Abstracts of Reports at the All-Republic Conference on the Applications of Polymeric Materials in the National Economy), Nalchik, 1978, No. 5, p. 14.
19. N. K. Vinogradova, Ts. L. Gelashvili, I. V. Zhuravleva, M. M. Teplyakov, and S. A. Pavlova, "Tezisy Dokladov Respublikanskoi Konferentsii po Primeneniyu Polimernykh Materialov" (Abstracts of Reports at the All-Republic Conference on the Applications of Polymeric Materials), Nalchik, 1977, No. 4, p. 16.
20. V. V. Korshak, M. M. Teplyakov, and V. P. Chebotarev, J. Polymer Sci., Polym. Letters, 11, 589 (1973).
21. V. V. Korshak, M. M. Teplyakov, V. P. Chebotarev, V. A. Li, and V. M. Kalinin, Izv. Akad. Nauk SSSR, Ser. Khim., 1091 (1973).
22. M. M. Teplyakow and V. P. Tschebotarjow, Acta Chim. (Budapest), 81, 281 (1974).
23. V. P. Chebotarev, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1973.
24. B. V. Rozynov, M. M. Teplyakov, V. P. Chebotarev, and V. V. Korshak, Izv. Akad. Nauk SSSR, Ser. Khim., 1602 (1974).
25. E. E. van Tamelen and I. L. Burkoth, J. Amer. Chem. Soc., 89, 151 (1967).
26. V. V. Korshak, M. M. Teplyakov, V. P. Chebotarev, and V. A. Li, Trudy Moskov. Khim.-Tekhnol. Inst. im. Mendeleeva, 70, 158 (1972).
27. V. P. Chebotarev, M. M. Teplyakov, and V. V. Korshak, Izv. Akad. Nauk SSSR, Ser. Khim., 1407 (1974).
28. V. V. Korshak, M. M. Teplyakov, and V. P. Chebotarev, Vysokomol Soed., A16, 497 (1974).
29. N. V. Karyakin, V. N. Sapozhnikov, M. M. Teplyakov, and V. P. Chebotarev, Dokl. Akad. Nauk SSSR, 237, 867 (1977).
30. N. V. Karyakin, V. N. Sapozhnikov, M. M. Teplyakov, and V. P. Chebotarev, Vysokomol. Soed., A20, 1950 (1978).
31. V. V. Korshak, "Raznozvennost' Polimerov" (The Heterounit Nature of Polymers), Izd. Nauka, Moscow, 1977, p. 91; V. V. Korshak, J. Prakt. Chem., 312, 422 (1971).
32. N. V. Karyakin, V. N. Sapozhnikov, and N. B. Rabinovich, Trudy po Khim. i Khim. Tekhnol., Gor'kii, No. 2, 147 (1972).
33. D. M. Kakauridze, V. P. Chebotarev, V. A. Kim, A. I. Efim'ev, N. V. Kravchenko, M. M. Teplyakov, and V. V. Korshak, "Tezisy Dokladov Nauchnoi Konferentsii po Khimii i Fizike Polimerov" (Abstracts of Reports at the Scientific Conference on the Chemistry and Physics of Polymers), Nalchik, 1973, p. 36.
34. V. V. Korshak, M. M. Teplyakov, V. P. Chebotarev, I. A. Khotina, and D. M. Kakauridze, Preprints at the XXIIIrd International Symposium on Macromolecules, Madrid, 1974, Vol. 1, p. 284.
35. D. M. Kakauridze, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1975.
36. V. V. Korshak, M. M. Teplyakov, D. M. Kakauridze, and N. V. Kravchenko, Dokl. Akad. Nauk SSSR, 219, 117 (1974).
37. M. V. Shishkina, M. M. Teplyakov, V. P. Chebotarev, and V. V. Korshak, Vysokomol. Soed., A17, 1510 (1975).

38. V. V. Korshak, M. M. Teplyakov, I. A. Khotina, and V. P. Chebotarev, Vysokomol. Soed., **B17**, 504 (1975).
39. V. V. Korshak, M. M. Teplyakov, D. M. Kakauridze, D. A. Shapiro, and E. L. Vulakh, Vysokomol. Soed., **A18**, 1831 (1976).
40. M. V. Shishkina, M. M. Teplyakov, V. P. Chebotarev, and V. V. Korshak, Makromol. Chem., **175**, 3475 (1974).
41. S. A. Pavlova, G. I. Timofeeva, V. V. Korshak, D. M. Kakauridze, and M. M. Teplyakov, Vysokomol. Soed., **B17**, 909 (1975).
42. V. V. Korshak, M. M. Teplyakov, T. L. Gelashvily, S. N. Komarov, L. I. Zaharkin, and V. N. Kalynin, J. Polymer. Sci., Polym. Letters. (in the Press).
43. V. V. Korshak, V. A. Sergeev, and M. M. Teplyakov, BRD P. 2 106 396 (1978).
44. V. V. Korshak, M. M. Teplyakov, and V. P. Chebotarev, USSR P. 416 369 (1974); Byul. Izobret., No. 7, 78 (1974).
45. I. A. Gribova, V. A. Sergeev, V. V. Korshak, A. P. Krasnov, V. K. Shitikov, M. M. Teplyakov, G. V. Elerdashvili, G. I. Gureeva, and R. A. Dvorikova, "Tezisy Doklada Nauchno-Tekhnicheskoi Konferentsii 'Primenenie Kompozitsionnykh Polimernykh Materialov v Narodnom Khozyaistve'" (Abstracts of Reports at the Science and Engineering Conference on 'The Application of Composite Polymeric Materials in the National Economy'), Gomel, 1974, p. 9.
46. V. V. Korshak, M. M. Teplyakov, and I. A. Khotina, Vysokomol. Soed., **B20**, 370 (1978).
47. V. V. Korshak, M. M. Teplyakov, and I. A. Khotina, USSR P. 608 817 (1978); Byul. Izobret., No. 20 (1978).
48. A. N. Nesmeyanov, N. N. Rukhlyada, E. V. Leonova, N. S. Kochetkova, and N. V. Bychko, USSR P. 494 397 (1974); Byul. Izobret., No. 45 (1975) p. 67.
49. A. V. Dmitrenko, K. A. Bychko, and M. M. Teplyakov, "Tezisy Dokladov Respublikanskoi Konferentsii po Primeneniyu Polimernykh Materialov v Narodnom Khozyaistve" (Abstracts of Reports at the All-Republic Conference on the Applications of Polymeric Materials in the National Economy), Nalchik, 1977 No. 4, p. 19.
50. M. M. Teplyakov, A. V. Dmitrenko, V. A. Dyatlov, and I. V. Blagodatskikh, "Tezisy Dokladov Respublikanskoi Konferentsii po Primeneniyu Polimernykh Materialov v Narodnom Khozyaistve" (Abstracts of Reports at the All-Republic Conference on the Applications of Polymeric Materials in the National Economy), Nalchik, 1978, No. 5, p. 5.
51. M. M. Teplyakov, A. V. Dmitrenko, and K. A. Bychko, "Tezisy Kratkikh Soobshchenii Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii" (Abstracts of Brief Communications at the International Symposium on Macromolecular Chemistry), Tashkent, 1978, Vol. 3, p. 81.

Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow