

Zależność temperatury zeszklenia polimerów od czasu reakcji

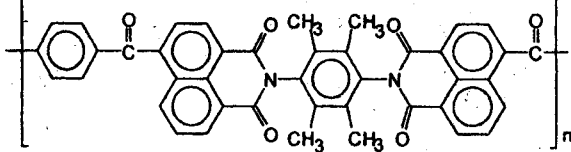
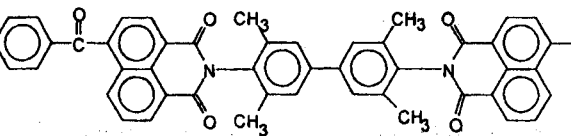
Struktura polimerów	Tg [°C] po czasie reakcji		
	24 [h]	48 [h]	100 [h]
	192	296	404
	271	289	-

Tabela przedstawia wzrost temperatury zeszklenia polimerów w zależności od czasu prowadzenia syntezy.

Ponieważ wydłużanie czasu reakcji wpływa bardzo niewiele na wzrost lepkości zredukowanej polimeru, obserwowany wzrost Tg wynika najprawdopodobniej z zachodzenia procesu cyklodehydratacji powodującego obniżenie elastyczności łańcucha polimeru.

Tak więc polinaftalimidy otrzymane z diamin aromatycznych zawierających w pozycji orto do grupy aminowej podstawniki alkilowe mające przy węglu  $\alpha$  dwa atomy wodoru, mogą być prekursorami nowej grupy termoodpornych semidrabinkowych polimerów - polinaftoilenobenzopiroli.

## POLYMER - CHLORAL DERIVATIVES THE MOST EFFECTIVE FIRE- SAFE MATERIALS

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Розглянуті хлорохідні епоксидних смол, поліуретанів і полісульфонатів і способи їх практичного використання.

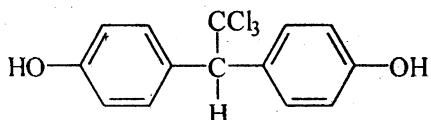
Chlore derivatives of epoxy resins and polysulfonates have been considered and also the ways of their practical applications have been shown.

### Introduction

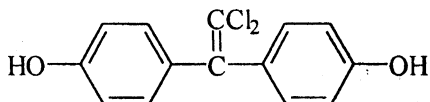
Bisphenolic polymers such as epoxy resins, polycarbonates, polysulphones and polyarylates are well known. All these polymers due to their structure characterized by high number of aromatic rings joined by aliphatic "hinges" possess

very good properties, especially dielectric ones, as well as fairly good chemical and thermal resistance and are suitable for thermoplastic processing. [1]. The special polymer research group led by the author at the Warsaw University of Technology, has carried out considerable work on the synthesis, properties and application of new bisphenolic polymers. [2] The importance of these works have been also recognized abroad [3, 4, 5]. In 1948 the Nobel Prize was awarded to Paul Muller in the field of physiological and medical research for the discovery of DDT, which has released mankind from a number of plagues such as malaria and disease carrying insects. Chloral is an intermediate product for DDT production. On account of its toxicological effects and the insects immunization against it, DDT was withdrawn from production. As a consequence of this the utilization of chloral presents a technological and experimental problem which is a subject of research.

Extensive investigations into the utilization of chloral - and its derivatives - for polymer synthesis have been carried out at the Technical University in Warsaw for the last 40 years.[6, 7, 8]. There are also important developments in other places [9, 10, 11]. These works are connected with the growing industrial requirements for fire - proof and self - extinguishing materials. The most interesting of these is 2,2-bis(p-hydroxyphenyl) 1,1 - dichloroethylene. In 1962 was applied first Polish patent [12] and in 1965 author got his PhD on new self - extinguishing epoxy resins. In 1965 was published first report on polycarbonates [13] in the mid seventies on polyarylates [14, 15] and polysulphones. [16]. Next papers and patents were connected with polyurethanes [17] vinyl - ester resins [18], polysulphonates [19] and UV-sensitive versions of bisphenolic polymers.[20, 21]. In 1988 author got his Sc.D. on new polymers - chloral derivatives [1]. In the seventies pilot productions on chlorobisphenols epoxies, polycarbonates and polyarylate films were carried out in Poland. Now polymers chloral derivatives polish original invention are in the centre of interest in scientific and industrial circles. University of Massachusetts Amherst is carrying out intensive research in this field and big companies are almost ready to start production. It was proved that not expensive chloral polymers are very effective as fire - safe materials [22].



(I) chlorobisphenol I (CBP I)



(II) chlorobisphenol II (CBP II)

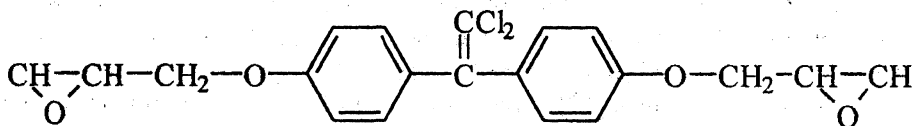
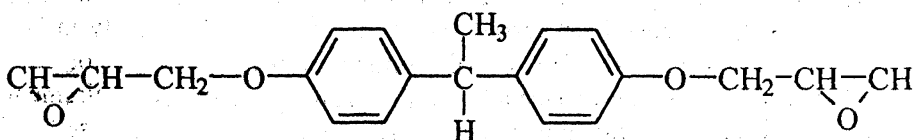
#### The formulas of chlorobisphenols

The above presented monomers are mainly used in our research. CBP II fulfills demands for thermal and chemical resistance together with good dielectrical properties. CBP I used mainly in the case of epoxy resins gives very good fire-resistance.

This paper is limited in presentation to epoxy resins, their applications and polyarylesters: polyarylates and polysulphonates. The examples of UV-sensitive versions are also presented.

### EPOXY RESINS AND APPLICATION

Below are chemical structures of the epoxy resins derived from chlorobisphenol I and chlorobisphenol II. The amount of chlorine in epoxy resins based on chlorobisphenol I reaches 25% before curing. After curing it is slightly reduced but it always stays above 15%, depending on the amount of curing agent and the type of resins, which ensures very good self-extinguishing properties of this kind of resins.



(III) and (IV)

The formulas of bisglycidyl ethers of chlorobisphenols

The resins based on chlorobisphenols were hot-cured using acid anhydrides such as phthalic acid anhydrides, or after some modifications also cold cured using aliphatic amines.

The thermal resistance of resins based on chlorobisphenol I is about 30% higher than of analogous resins obtained from Bisphenol A. The heat resistance, depending on the method employed, reaches 130-165°C. Mechanical properties are good, generally better than those of conventional resins. A number of properties is higher than those of epoxy resins based on Bisphenol A (dian) produced for a long time in Poland. As it is shown in Tables 1 and 2 the resins based on chlorobisphenol II have a higher thermal resistance than the resins based on chlorobisphenol I.

Table 1

Physic-Chemical Properties	Thermal Resistance of Resins		
	M	CBP I Epoxy Resin	CBP II Epoxy Resin
1. outlook		solid resins of light green	to deeply brown colour
2. epoxy groups	%	17-18	19-22
3. softening temp	°C	50-60	20-30
4. content of insoluble in acetone parts	%	0,03	0,03
5. chlorine contents	%	25,3	21,4

Table 2

## Mechanical Properties of Resins

Physic-Mechanical Properties	M	Epoxy resins based on	
		CBP I	CBP II
1.thermal resistivity by Martens	°C	132	148
2.softening temp. by Vicat	°C	172	181
3.hardness by Brinell	kg/cm <sup>2</sup>	25,9	22,2
4.bending strength	kg/cm <sup>2</sup>	1089	1290
5.impact strength by Charpy	kg/cm <sup>2</sup>	15,9	19,0
6.self-extinguishing	Sec	1	3

## CBP I as vulcanizing agent

Vulcanization of butadiene rubber (BR) with bisglycidyl ether of 2,2-bis (p-hydroxy-phenyl)-1,1,1-trichloroethane (BGE) yielded modified vulcanizates with slightly improved oil resistance, as well as slightly lowered glass transition temperature and significantly fewer changes in properties during thermo - oxidative aging. The highest crosslinking efficiency of this simultaneous vulcanizing and modifying agent was found at a concentration of 5 weight parts per 100 weight parts rubber (phr).

BGE was found to be an efficient crosslinking (vulcanizing) agent for butadiene rubbers. At the same time, it acts as a rubber modifier. The simultaneous vulcanization and modification of BR with BGE leads to a slight increase in oil resistance and likewise, to a slight decrease in glass transition temperature, but it significantly suppresses changes of vulcanizate properties during thermo - oxidative aging. The optimum BGE concentration, from the point of view of its crosslinking efficiency, is 5 phr.

The influence of N, N-diphenylguanidine (DPG), salicylic acid (SA), and thiourea (TU) on the kinetics and ultimate extent of butadiene rubber (BR) vulcanization with bisglycidyl ether of 2,2-bis(p-hydroxyphenyl)-1,1,1-trichloroethane (BGE) have been investigated. DPG has practically no influence on the course of vulcanization. SA increases its rate significantly. TU decreases activation energy as well as the ultimate extent of crosslinking. On the basis of these experimental results the mechanism of BR vulcanization with BGE is discussed. It is probable that the mechanism is mixed. Cationic initiation is followed by radical crosslinking reactions.

Studies of properties of styrene-butadiene, styrene-acrylonitrile, and butadiene rubbers crosslinked with bisglycidylether of 2,2-bis(p-hydroxyphenyl)-1,1,1-trichloroethane (BGE) have shown that BGE acts not only as a crosslinking agent but also as a rubber modifier. The simultaneous vulcanization and modification of BR with BGE leads to a slight increase in oil resistance and likewise, to a slight decrease in glass transition temperature, but it significantly suppresses changes of vulcanizate properties during thermo - oxidative aging.

In the initial steps of BR vulcanization with BGE, characterized by the rate of crosslinking, mainly ionic reactions take place, according to the proposition of Brzozowski and co-workers/23/. This view is supported by the accelerating effect of salicylic acid which leads to the proposition of cationic mechanism of the cure initiation. In the next steps (propagation), characterized by the ultimate extent of

crosslinking, mainly radical reactions take place, also according to the proposition of Brzozowski and co-workers/24/.

This view's supported not only by the diminishing effect of thiourea, which is known as a radical scavenger, on the ultimate extent of crosslinking, but also by the high value of activation energy of vulcanization and by its decrease in the presence of thiourea.

Table 3

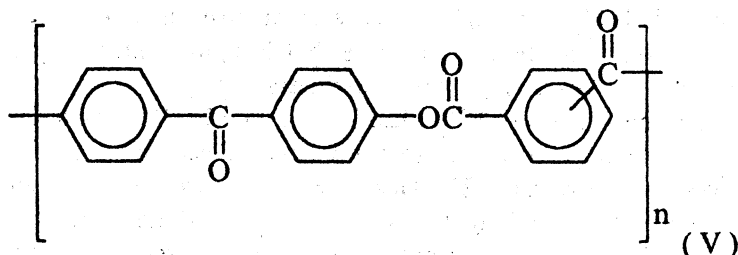
**Influences of N, N-dipheylguanidine, salicylic acid, and thiourea on the activation energy and the ultimate extent of butadiene rubber vulcanization with BGE**

Rubber compound formulation (weight parts)	0	DPG	SA	TU
Batadiene rubber (SKD)	100	100	100	100
BGE	5	5	5	5
N, N - diphenylguanidine	-	1	-	-
Salicylic acid	-	-	1	-
Thiourea	-	-	-	1
Activation energy of vulcanization (kJ/mole)	138	138	138	62
Ultimate extent of crosslinking (kPa)	245	240	24	14

#### FIRE-RETARDANT POLYARYLATES

The first mentions of the polyarylates date back to the tum of fifties and sixties of the century. These polymers were obtained by Gevaert in Belgium and Eastman Kodak in USA. The very intensive development of polyarylate research was observed in the Soviet Union where a wide range of technology and research was conducted. Worth mentioning were the results obtained by Professor Korshak in Moscow. The polyarlates exhibit good physico-mechanical properties, thermostability, high resistivity to aggressive chemicals, good (better than those of polyterephthalic polymers and polycarbonates) dielectric properties, and are characterized by high softening temperatures. Polyarylates of dicarboxylic aromatic acids are good as foil and fibre-forming polymers. Because of these properties polyarylates have many applications as parts of machines working at high temperatures, thermoresistant electroinsulating coatings and foils, fibres and foam plastics, adhesives and lacquer coatings.

In Poland the research on the self-extinguishing polyarylates has been successfully carried out. Such polyarylates are obtained from chlorobisphenol II. Chemical structure of these polyarylates is illustrated below:



The reaction goes interfacially at room temperature for polymers based on CBP II. Analysis of the data tables 4 and 5 proves that replacement of dian by chlorobisphenols in analogous polymers changes advantageously all the parameters and increases the general properties of the discussed polymers. Particularly good results are obtained when chlorobisphenol II is used as a substrate for polycondensation. The polyarylates containing chlorobisphenol II have much higher thermoreactivity and dielectric properties. Dielectric loss factor of these polyarylates has the lowest value of all examined polymers and while increasing temperature from 25 to 180 °C its value is almost the same.

Table 4

Properties	Miscellaneous Properties		
	Bisphenol A	Polyarylate based on CBP II	Polyarylate based on CBP II (cond.)
Absolute viscosity 25°C tetrachloroethane	1.88	1.72	----
thermal resistivity °C	330	360	360
foil tensile strenght	820	850	890
foil break elongation %	8	10	18
Combustibility	hardly combustible	incombustible self-extinguishing	incombustible self-extinguishing

The increase of reduced viscosity value for CBP II polymers indicates higher molecular weight and so the increase of foil-and fiber-forming properties. The value properties of polyarylate foils are the high value of specific volume resistivity, dielectric const. and strong self-extinguishing effect, in table. We obtained polyarylates as polymers and foils, on a large-laboratory scale.

Table 5

## Dielectric Properties of Par C-2 Foil

Temp.	Surface resistivity Polish Standards PN-61/E-04405	Volume Resistivity Polish Standards PN-61/E-04405	Dielectric Constant Polish Standards PN-69/E-04405			Dielectric Loss Factor Polish Standards PN-69/E-04405			Dielectric Strength Polish Standards
			A	B	B	0,08	1 kHz	10	
			kHz	1 kHz	kHz	kHz	kHz	kHz	
20°C	1.6 10 <sup>16</sup> Ω	1.7 10 <sup>16</sup> Ω cm	3,36	3,34	3,31	2,9	3,0	3,1	200 kV/mm
100°C	1.6 10 <sup>16</sup> Ω	2.9 10 <sup>14</sup> Ωcm	3,26	3,34	3,21	1,9	2,0	2,0	----
150°C	3.2 10 <sup>16</sup> Ω	2.3 10 <sup>13</sup> Ω cm	-	-	-	2,3	3,0	3,3	----
180°C	----	----	2,83	2,79	2,80	2,5	3,3	3,7	----
200°C	----	4.4 10 <sup>12</sup> Ωcm	2,71	2,61	2,69	-	-	-	----

The polyarylate foil is applicable in the electronic and radiotechnical industry and as a construction material for precision instruments and electric equipment. Polyarylates can be deposit on the surface as coatings, basic materials for flexible thermally stable printed circuits, flexible diaphragms and membrane. They are as follow:

- max. service temperature long term - 180°C

- max. service temperature short term - 260°C
- resistance to low temperatures : at - 70°C foil retains fully elastic and flexible
- beginning of thermal decomposition in air DTA data 360°C
- weight loss after heating for 150 hrs at 200°C 1%

The dielectric and mechanical properties don't change after 1000 hours heating at 180°C.

Our present research work indicates that there is the possibility of annealing the polyarylate foils based on chlorobisphenol II. The foil sample heated 2-5 hrs. at 180-250°C has a definitely higher chemical resistivity. It is especially interesting that the annealed foil is insoluble in chlorinated aliphatic hydrocarbons which are the best solvent for use in the foil - forming process. Table 12 gives the more interesting features of annealed and unannealed polyarylate foils based on chlorobisphenol II. Data on polyarylate foil based on Bisphenol A are included for comparison (table 11 and 12). table 14 illustrates the differences in molecular weight and properties of polyarylates based on chlorobisphenols obtained by two methods: polycondensation with the addition of emulsifying agent - column A and without the addition of emulsifying agent - column B. It is clear that when no emulsifying agent was used better results were obtained. The difference in dielectric properties of annealed polyarylates is clearly shown in Table 5.

Derivatograms of polyarylates illustrate the thermoresistivity of chlorobisphenolic polyarylates up to 360°C ( Bisphenol A polyarylate up to 330°C).

Table 6

Effect of MW on Physical Properties

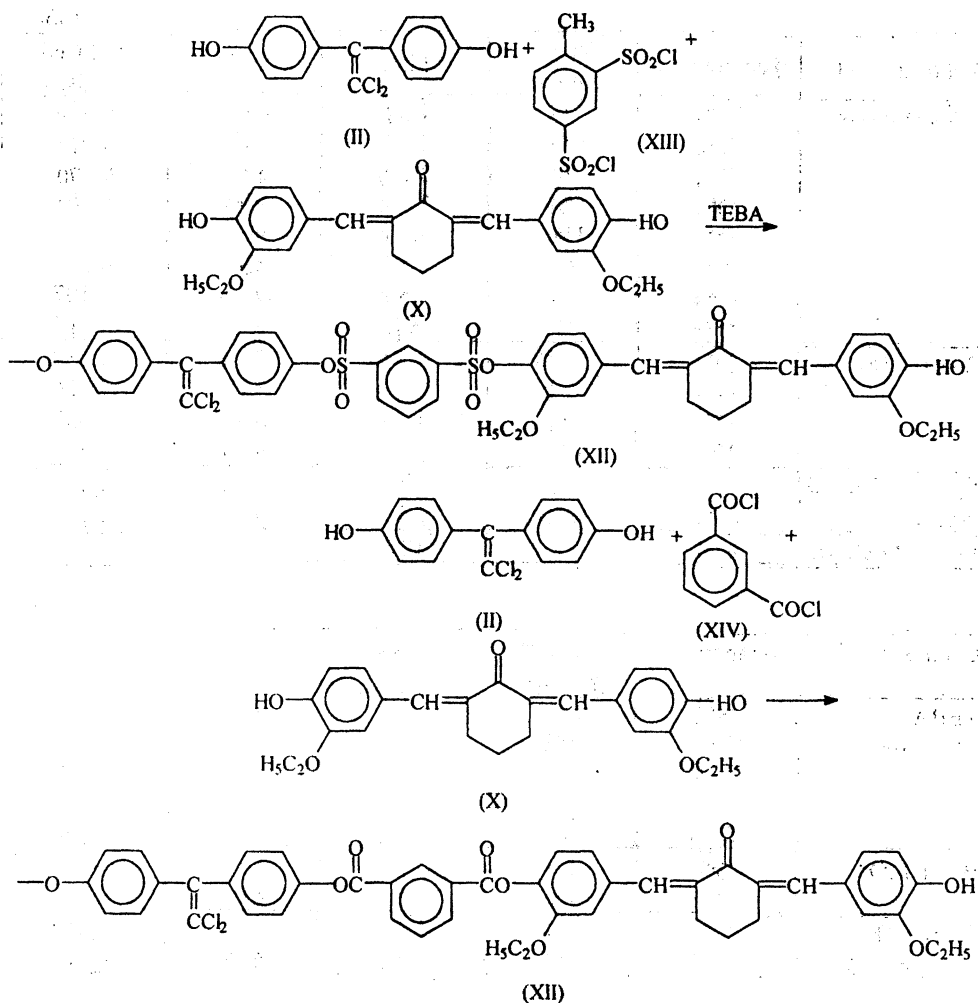
Properties	Polyarylate based on Bisphenol A		Polyarylate based on Chlorobisphenol II	
	A	B	A	B
n red.; c=0,5g/dcl t=25°C; tetrachloroethane dcl/g	1,31	2,65	1,10	2,32
n abs.;t=25°C; tetrachloroethane dcl/g	1,03	1,88	0,92	1,72
molecular weight	102000	231000	100000	249000
degree of polymerization	285	645	605	605

Table 6 illustrates the molecular weights measurements.

### POLYSULPHONATES

As a result of complex research work concerned with the utilization of chloral's derivatives in the synthesis of polymers, the proposition of using them to synthesize new fire-resisting polysulphonates was taken into consideration.

New fire-resisting polysulphonates of the general formulas /VIII, IX/ were obtained by interfacial polycondensation of 2,2-bis/p-hydroxyphenyl/1,1-dichloroethylene /III/ and 2,2-bis/p-chlorosulphonyl/1,1 dichloroethylene /VI/ respectively in the presence of catalyst mentioned in the tables below.



The monomer /II/ was obtained through the condensation of phenol with chloral in the presence of  $H_2SO_4$  and subsequent dehydrochlorination, and special purification.

The monomers /VI, VII/ were obtained through the condensation of chloral with benzene or 4-methoxybenzene respectively and further chlorosulphonation of their dehydrochlorinated derivatives.

The parameters of polycondensation were investigated and the following conditions were to be optimum:

- water phase concentration -  $0,2 \text{ mol/dcm}^3$
- organic phase concentration -  $0,4 \text{ mol/dcm}^3$

Several polycondensation reactions have been carried out. The results including the kind of catalyst, reaction temperature, the amount of catalyst, the time of reaction, the yield, the reduced viscosity are shown in the table I /for polymer I/ and in the table II /for polymer II/. The amount of catalyst were used in weight percents due to total weight of monomers.



Table 7

Catalyst Used	Temperature	Catalyst amount	Time	Yield	Reduced viscosity
Teba chloride	25%	2%	3,5 h	69%	0,410
	25%	3,5%	3,5 h	75%	0,641
	25%	5%	3,5 h	82%	0,890
	25%	7%	3,5 h	92%	1,103
	25%	15%	3,5 h	93%	1,017
	5%	7%	3,5 h	83%	0,355
	35%	7%	3,5 h	92%	1,107
	25%	7%	5 h	93%	1,112
Bu <sub>4</sub> NHSO <sub>4</sub>	25%	3,5%	3,5 h	75%	0,532
	25%	5%	3,5 h	88%	0,786
	25%	7%	3,5 h	91%	0,832
	25%	15%	3,5 h	92%	0,838
Crown ether 15 crown - 5	25%	5%	3,5 h	83%	0,325
	25%	7%	3,5 h	85%	0,401
Without catalyst	25%	0	12 h	35%	0,19

Table 8

Catalyst used	Temperature	Catalyst amount	Time	Yield	Reduced viscosity
TEBA Bromide	25%	3,5%	3,5 h	25%	0,907
	25%	5%	3,5 h	58%	1,040
	25%	7%	3,5 h	75%	1,209
	25%	10%	3,5 h	83%	1,213
	25%	15%	3,5 h	91%	1,232
Bu <sub>4</sub> NHSO <sub>4</sub>	25%	5%	3,5 h	60%	0,62
	25%	7%	3,5 h	82%	0,98
Crown ether 15 crown - 5	25%	5%	3,5 h	38%	0,352
	25%	7%	3,5 h	62%	0,423

IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra confirmed the structure of the polymers given above. The beginning of decomposition temperature and maximum decomposition temperature for polymer VIII, we found to be 305°C and 363°C respectively from derivatographic analysis. The same data for polymer IX are 300°C and 359°C. Oxygen index according to ASTM-D-2863-70 are estimated to be 95 for polymer VIII and I and 70 for polymer IX.

### Conclusions

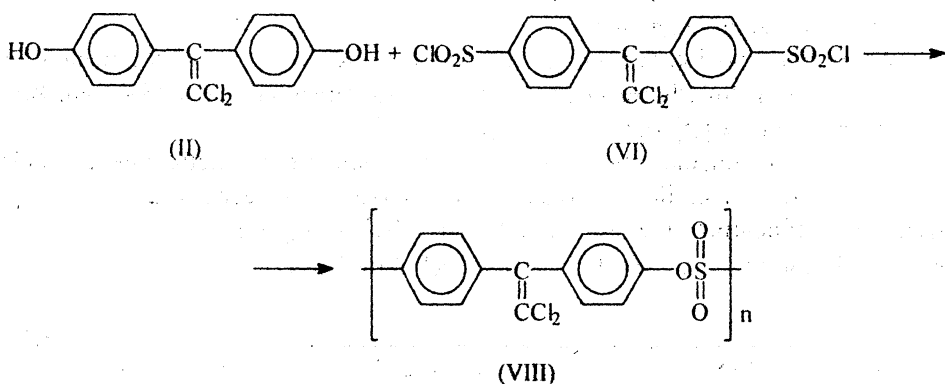
1. The most efficient of interphase catalyst was found to be TEBA /bromide or chloride/.
2. The optimum polycondensation conditions were found to be as follows:
  - aqueous NaOH phase concentration 0,2 mol/dcm<sup>3</sup>
  - methylene chloride phase concentration 0,4 mol/dcm<sup>3</sup>
  - amount of catalyst 7% for polymer I and 10-15% for polymer IX
  - temperature 25°C
  - reaction time 3,5 h

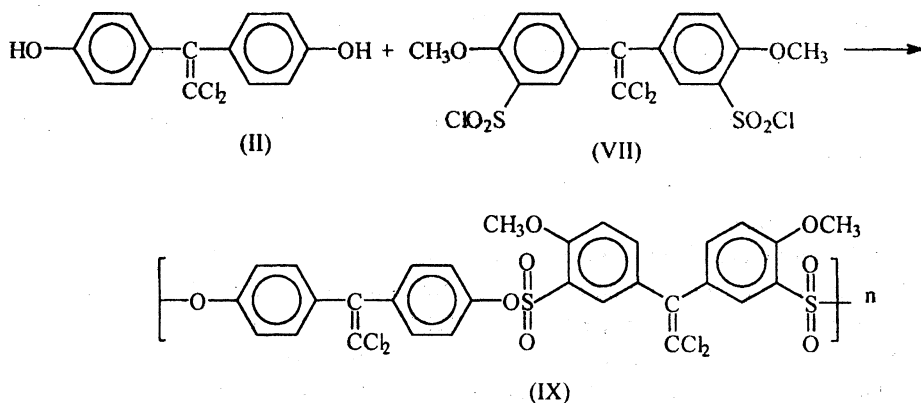
3. The raw materials used to obtaining of monomers are industrially available, for example bis /4-metoxyphenyl/trichloroethane is well known as very effective pesticide.
4. The thermoplastic properties and moldability of obtained polymers are found to be fairly good.
5. The polymers have high percentage of chlorine and sulphur giving them the fire-proofing properties.
6. The polymers were also tested as a paint binder and due to very high oxygen index, they could find application in fire-retardent paints, alone or as an additive.

The preparation and properties of polyarylesters based on chlorobisphenols have been carried out in Warsaw Technical University for many years /1-2/. Preliminary works on UV-sensitive polyarylesters including chlorobisphenol have been already done /3-5/. This paper is a continuation of previous works.

### UV - sensitive polyarylesters

UV-sensitive polyarylesters /XI, XII/ were obtained by interfacial polycondensation. The aqueous phase was an alkali solution of bisphenols while the organic phase was 2,4-bis/chlorosulphonyl/toluene /XIII/ or isophthaloyl/chloride/XIV/ dissolved in methylene chloride. UV - sensitive bisphenol obtained by condensation of ethylvaniline /3-ethoxy 4-hydroxybenzaldehyde /with acetone, urea, cyclohexanone were used together with 2,2 bis/p-hydroxyphenyl/2,2 dichloroethylene /II/ as the nonsensitive bisphenol. The best results were obtained in the case of bis-/3-ethoxy-4-hydroxybenzylidene/ cyclohexanone /XV/ and this bisphenol was further investigated. The polycondensation was carried out at room temperature in the presence of triethylbenzylammonium chloride /TEBA/.





On the drawings are presented fragments of obtained polymers /XI/ and /XII/. 2,4 bis/chlorosulphonyl toluene /III/ was obtained by direct chlorosulphonation of toluene. The crude product was crystallized in hexane].

Isophatoyl chloride /XIV/ was obtained from Fluka AG. 2,2 bis /4-hydroxyphenyl/ 1,1 dichloroethane /II/ was obtained as described in the literature. Bis-/3-etoxy 4-hydroxybenzylidene/-cyclohexanone /X/ was obtained by the condensation of ethylvaniline with cyclohexanone in the presence of HCl gas. The crude product was crystallized in aqueous ethanol.

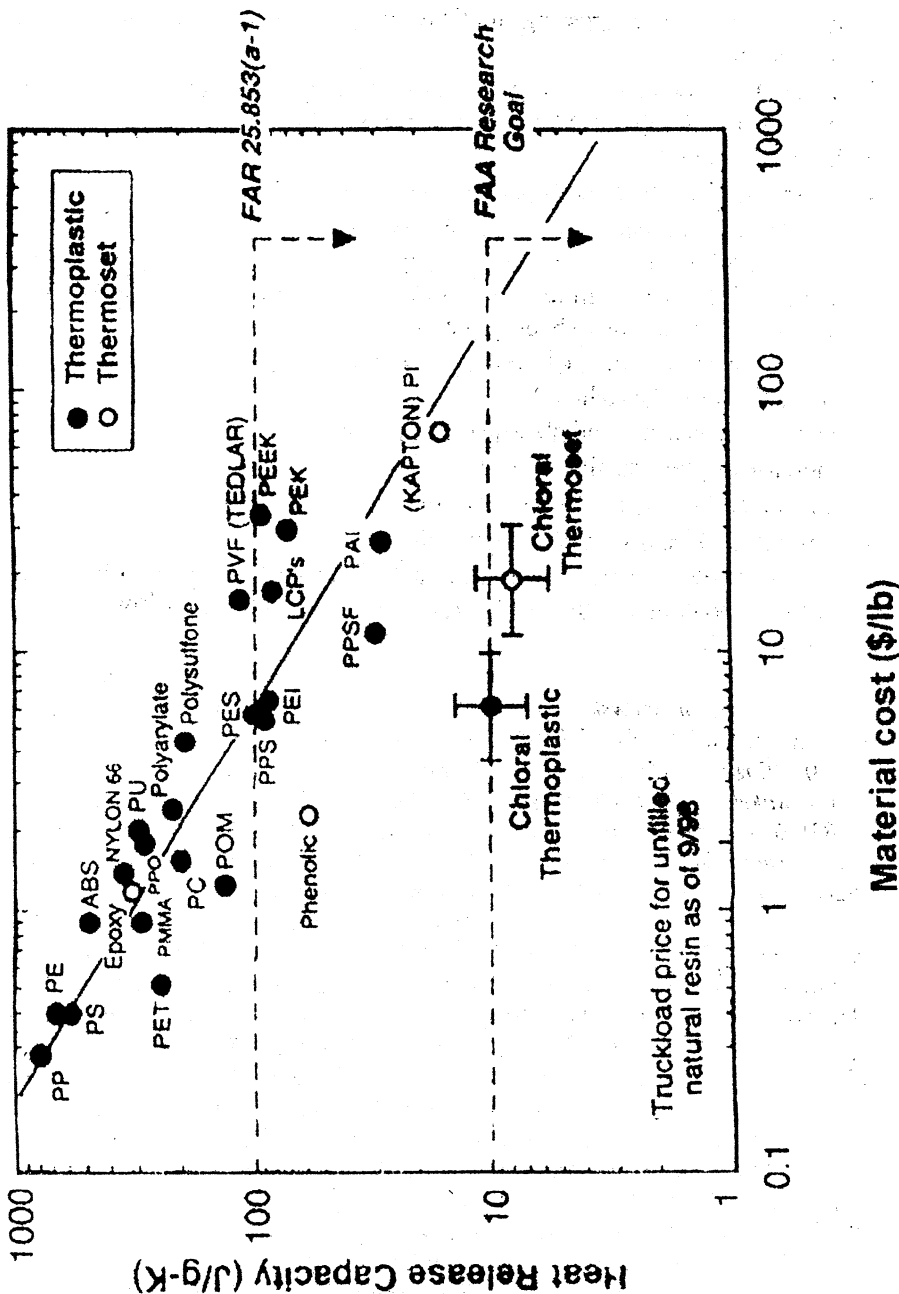
Several polycondensation reactions have been carried out. The results including the amounts of UV-sensitive bisphenols, the yield, intrinsic viscosity, temperatures of decomposition are shown in table I for polymer I and in table II for polymer II.

1. UV/VIS and IR spectra confirms the estimated structures of used monomers and obtained UV-sensitive polymers.
2. The maximum absorbtion band for polymers /I/ is 340 nm and as expected the absorbtion field is directly dependent on the % molar amount of UV-sensitive monomers used in the polycondensation.
3. The obtained UV-sensitive polymers are easy soluble in methylene chloride, tetrachloroethane and similar solvent and be used as photoresist coatings.
4. The adhesion of coating on glass was found to be fairly good.
5. The resolution of our photoresist coatings is below 5  $\mu\text{m}$ .

Table 9

% mol of bisphenols		Yield %	Intrinsic viscosity 100 ml/g	Decomopstion temperature°C
Bisphenol /VI/	Bispheno /V/			
1,00	100	70	0,20	295
2,5,	95	85	0,23	-
3,1,	90	85	0,32	-
4,20	80	83	0,34	-
5,30	70	85	0,36	230
6,50	50	89	0,34	-
7,75	25	84	0,28	-
8,10	0	83	0,32	230

# MATERIAL COSTS AND FIRE SAFETY



## GENERAL CONCLUSIONS

1. The research conducted at the Warsaw Technical University of Technology shows the great possibilities existing in the field of bisphenolic polymers of designing materials with new special functions giving them new properties and applications.

2. The main application of both chlorobisphenols were epoxy resins with very good properties. Very interesting application is using them as vulcanizing agent for diene rubber.
3. The main advantages of utilizing interfacial polycondensation to obtain polyarylates and polyarylosulphonates are as follows:
  - high reaction rate;
  - room temperature, pressureless reaction;
  - possibility of using monomers sensitive to high temperatures.
4. The mechanism of interfacial polycondensation of polyarylates has been estimated and crystalline ion pairs consisting of a bisphenolate anion and an ammonium cation have been isolated.
5. The specific structure of chlorobisphenol (II) gives the polymer the following advantages over Bisphenol A:
  - increase of thermal and chemical resistance;
  - increase of glas-transition point;
  - considerable decrease in flammability;
  - possibility of thermal crosslinking at 200°C.
6. Last investigation carried out in Massachussets University Amherst proved that chloral polymers are most effective fire-safe materials. Below it was graphically presented (22).

1. Z.K. Brzozowski - ScD desertation ( habilitation), Warsaw University of Technology Edition, Nr 37(1986). 2. Z.K. Brzozowski - *Polimery* 29, 10-11-12, 415-421 (1984) (English). 3. Factor, C.M. Orlando: *J.Polym. Sci. Chem.* 18, 79 (1980). 4. A.K. Mikutajew, E.R. Kocharsajewa, W.W. Korszak: *Wysokomol. Sojed., Seria B*, 25, 916 (1983). 5. P.W.Morgan: *Interfacial Synthesis - Recent Advances - Comments on the status and future of Interfacial Polycondensation*, M.Dekker, N.York 1982. 6. Z.K. Brzozowski: *Przem. Chem.*, 42, 283 (1963). 7. Z.K. Brzozowski : *Mat. XXIV IUPAC Congress Hamburg 1973*, p. 11 8. Z.K. Brzozowski, P. Karwowski, *Macromol. Report A* 32, 1263-1270 (1995). 9. Z. Wielgosz, S. Porejko: *Polimery* 17, 76 (1972). 10. V. Duchacek, A. Kuta, J. Simek, Z.K. Brzozowski, *J.Polym.Eng.*, 18, 361 (1998). 11. V. Duchacek, A. Kuta, J. Simek, Z.K. Brzozowski, *Proc. XIV Conference "Polymer Modification", Kudowa (Poland)*, 26-30.09.99, pp. 52-55 (1999). 12. Z.K. Brzozowski, S. Porejko: *Pat. PL 47344* (1962), *pat. UK 1051335* (1963), *pat. France. 1328377* (1963). 13. S. Porejko, Z.K. Brzozowski, S. Mączyński, Z. Wielgosz: *Chim. Ind.* 92 (3 bis), 243 (1964). 14. Z.K. Brzozowski, S. Porejko, J. Kielkiewicz, J. Kaczorowski : *pat. PL 76755*, *GDR 101687*, *USA 3887522*, *UK 1384972*, *FRG 2302709*, *France 2214718* (1971). 15. Z.K. Brzozowski: *J.Fire flammability- Fire Reterdant Chem. Suppl. 1*, 218 (1974). 16. Z.K. Brzozowski, G. Rokicki: *Polimery* 20, nr 8 (1975). 17. Z.K. Brzozowski, J. Kielkiewicz, B. Góraj, W. Kamiński: *pat. PL 95033*, *Belg 833371*, *Italy 1062481*, *Iran 15552*, *USA 4163087* (1980). 18. Z.K. Brzozowski, A. Nowicki, *J. Polym. Sci., Part A-1* 13, 1479 (1975). 19. Z.K. Brzozowski, R. Kamiński, *Macromol. Reports A* 31, 217-223 (1994). 20. Z.K. Brzozowski, B. Jóźwik, *Journal Photochemistry* 35, 341-352 (1986). 21. K. Noniewicz, Z.K. Brzozowski, I. Zadrozna, *J Appl. Polym. Sci.* 60, 1071-1082 (1996). 22. R. Farris et al. *Mass.Univ. Amherst private comm.* (1999). 23. Z.K. Brzozowski, M. Gajewski and Z. Brzeziński, *J Appl. Polym. Sci.* 21, 1783 (1977). 24. Z.K. Brzozowski, T. Brzozowska-Janiak, S. Porejko and T. Floriańczyk, *Polimery*, 17, 419 (1971).